SYNTHESIS OF TELECHELIC AND TRI-ARMED POLYMERS BY LIVING CATIONIC POLYMERIZATION(Dissertation_全文)

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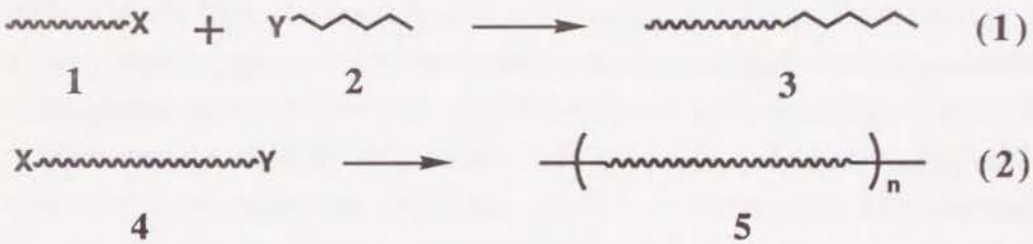
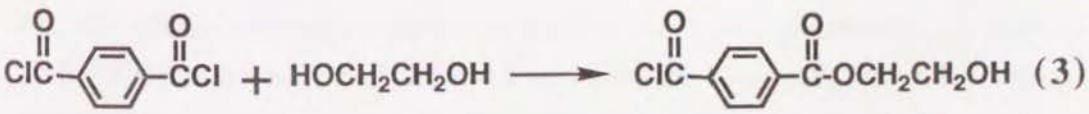
GENERAL INTRODUCTION

Background: Synthesis of End-Functionalized Polymers by Living Cationic Polymerization

End-Functionalized Polymers. "End-functionalized polymers" are a family of macromolecules that possess functional groups at their terminals. As in the reactions of small organic compounds, these terminal functional groups can react with each other to generate new polymer molecules where identical or different segments are connected through newly formed chemical bonds. For example, Eq (1) shows reaction of two different monofunctional end-reactive polymers (**1** and **2**; with terminal functions X and Y, respectively) into an AB-block copolymer (**3**), whereas Eq (2) illustrates a consecutive linking reaction of bifunctional telechelic polymers (**4**; with mutually reactive two different groups X and Y on both terminals) into a chain-extended polymer (**5**). As seen in these typical examples, end-functionalized polymers are versatile building blocks for the synthesis of new polymers.



Introduction of terminal functional groups into polymers may be achieved either by step polymerization (polycondensation or polyaddition) or by chain (addition) polymerization (ionic, radical, coordination, etc.). As exemplified in Eq (3), step polymerization affords, by definition, polymers with functional groups on both chain ends. Though mechanistically thus well-suited for quantitative end-



functionalization, however, step polymerization usually finds difficulty in control of the molecular weight and its distribution of the product polymers. On the other hand, conventional addition polymerization suffers frequent occurrence of chain transfer and termination reactions, which, in turn, lead to a mixture of ill-defined products where neither molecular weight control nor quantitative end-functionalization for specific terminal groups is possible.

Living Cationic Polymerization. In addition polymerization, therefore, controlled synthesis of end-functionalized polymers requires so-called "living" polymerization. "Living" polymerization is an addition polymerization reaction free from chain transfer and termination, in which the growing end thus remains active even after the complete consumption of monomers. These characteristics thereby allows living polymerization to yield end-functionalized polymers with well-defined terminal groups and controlled molecular weights.

First discovered by Szwarc in 1956,[1] living polymerization has extensively been exploited primarily in anionic polymerization of vinyl monomers. The growing carbanions therein, however, are susceptible to deactivation by polar functional groups in monomers as well as by electrophilic impurities and oxygen. Living anionic polymerization has therefore been confined to nonpolar hydrocarbon monomers, and in most cases it must be carried out in stringently purified systems, often under high vacuum, where traces of poisonous impurities and oxygen must be completely excluded. Because of the limited range of monomers and the laborious experimental procedures, living anionic polymerization has thus far been of rather limited applicability,[2] though indeed being well-suited for the synthesis of some end-functionalized polymers.

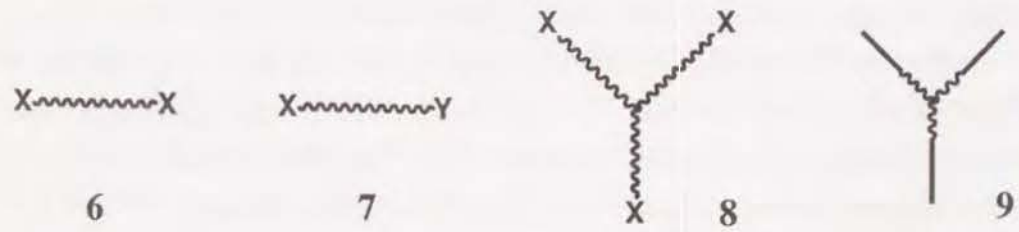
In contrast to the early discovery of its anionic counterparts, living cationic polymerization of vinyl monomers has been considered almost impossible, because the growing intermediates, namely carbocations, are inherently so unstable as to undergo numerous side-reactions, particularly chain transfer and termination. Starting in 1984 with vinyl ethers,[3a] however, Higashimura and his school have demonstrated that truly living cationic polymerization is indeed feasible through nucleophilic stabilization of the otherwise unstable growing carbocations.[4] The study by the Kyoto group has led to two principal methods for such carbocation

stabilization:[4] one by carefully designed *nucleophilic counteranions*[3] and the other by externally added mild *Lewis bases*.[5] It is now possible to obtain well-defined living cationic polymers from not only vinyl ethers but also *p*-alkoxystyrenes[6] and other related vinyl monomers.[4]

Importantly, living cationic polymerization has been shown to tolerate polar functional groups in monomers[4] as well as oxygen, and may be carried out routinely in conventional semi-open systems under dry nitrogen. Coupled with the large number (over 500) and the wide structural variety of cationically polymerizable monomers, these features thus provide living cationic polymerization with synthetic and operational advantages over the corresponding anionic processes; namely, it would prove highly versatile in the controlled synthesis of end-functional polymers from a variety of monomers, including those with functional polar pendant substituents, under conventional laboratory conditions.

Research Objectives: Synthesis of Telechelic and Tri-Armed Functional Polymers by Living Cationic Polymerization

Telechelic and Tri-Armed Polymers. In end-functionalized polymers, the backbones may be linear or branched (multi-armed); the terminal function(s) may be placed at one or all of the chain ends of a polymer molecule. Among numerous possible structures of end-functionalized polymers, particularly interesting are "telechelic" polymers (**6** and **7**) and "tri-armed" functional polymers (**8** and **9**).



6 **7** **8** **9**

Telechelic polymers,[2d] as their name implies [derived from *telos* (far) and *chelos* (claw) in Greek], carry identical (**6**) or different (**7**) functional groups at both ends of a linear backbone; thus, **6** and **7** may be coined *homo*telechelic and *hetero*telechelic polymers, respectively. **Tri-armed** end-functional polymers (**8**), on the other hand, are characterized by their radially extended architectures where three arm chains, each capped with a terminal functional group, are attached to a single core moiety. Extended versions of **8** include tri-armed block polymers (**9**), each arm chain of which consists of AB-type block segments. Through suitable reactions of their terminal functional groups, these bifunctional and trifunctional end-reactive polymers afford new polymers and products that cannot be prepared from their monofunctional counterparts nor by conventional chain polymerizations; examples include, among others, ABA-type and segmented multi-block polymers, chain-extended high polymers, three-dimensional networks, and amphiphilic polymer gels.

In this doctoral study, therefore, the author decided to pursue the synthesis of these telechelic and tri-armed functional polymers (**6**-**9**) of vinyl monomers. In view of the advantages over anionic processes discussed above, the author also decided to adopt living cationic polymerization as the basic methodology and to specifically employ vinyl ethers and *p*-alkoxystyrenes as monomers that give flexible and glassy backbones, respectively.

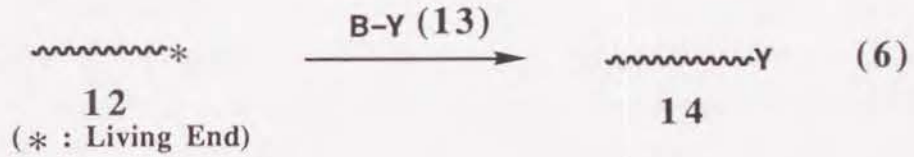
Synthesis of Telechelic Polymers by Living Cationic Polymerization. In general, living cationic polymerization offers two methods for end-functionalization of polymers.[7] In one method [Eq (4)], called "*functional initiator method*", living cationic polymerization is initiated with an initiator (**10**) carrying a functional group (X) to be incorporated into a polymer (**11**) as a "head" group (α-end). Herein a typical "functional initiator" is the adduct (**10a**) of a protonic acid with a vinyl ether with a pendant function X [Eq (5)]. By this method a series of monofunctional end-reactive poly(vinyl ethers) have been synthesized.[7,8]

The other method [Eq (6)], called "*end-capping method*", involves quenching of a living cationic polymer (**12**) with a nucleophilic reagent (**13**) having a functional group (Y) to be attached to a "tail" group (ω-end) of the product (**14**).[7] The end-capping reagents so far employed for poly(vinyl ethers) include amines,[9]

(4)

(5)

alcohols,[10] and the sodium salt of ethyl malonate (sodiomalonic ester).[8b] Obviously, combination of the end-capping method [Eq (6)] with the functional initiator method [Eq (4)] gives telechelic polymers (X~~~~Y), such as homotelechelic poly(isobutyl vinyl ether) with carboxyl groups (X = Y = COOH).[8b]



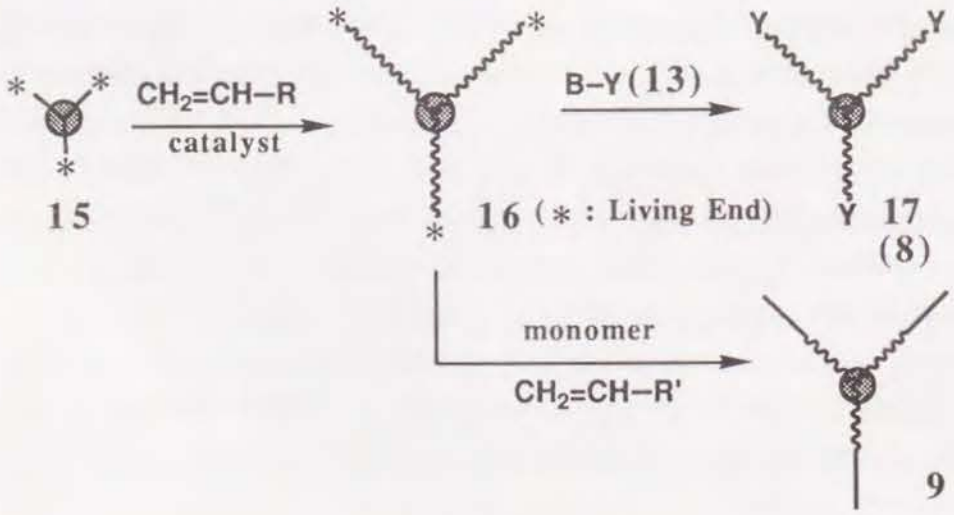
(6)

Despite these developments, however, the synthesis of end-functionalized polymers by living cationic polymerization has still been premature and incomplete. For example: (a) The living cationic polymerizations for these syntheses are carried out at low temperatures below -15 °C and have invariably been based on the stabilization of the growing carbocations with nucleophilic counteranions (see the preceding section). The other method, based on the stabilization by added Lewis bases, has not been employed yet, although this particular approach permits living cationic polymerization to proceed even at high temperature well above ambient. (b) Most of the previously reported examples are for vinyl ethers only. (c) No systematic studies are available thus far with regard to which types of functional

initiators [**10**; Eq (4)] as well as end-capping agents [**13**; Eq (6)] are suited. (d) The known telechelic poly(vinyl ethers) are only homotelechelic (**6**; X: COOH, etc.),[8b] heterotelechelic versions (**7**) being unknown.

Given these problems, the author therefore studied herein the synthesis of new homo- and hetero-telechelic polymers by living cationic polymerization. The primary focuses of the study included: (a) the utilization of living cationic processes based on the carbocation stabilization by added Lewis bases at high temperatures; (b) the synthesis of telechelic polymers from not only vinyl ethers but also *p*-alkoxystyrenes; and (c) the synthesis of not only homotelechelic (**6**) but also heterotelechelic polymers (**7**) with newly developed functional initiators and end-capping agents.

Synthesis of Tri-Armed Functional Polymers by Living Cationic Polymerization. Tri-armed polymers may be prepared by living cationic polymerization through the following route: living cationic polymerization is initiated with a trifunctional initiator (**15**), and the resulting trifunctional living polymer (**16**) is subsequently quenched with an end-capping agent (**13**) into the end-functionalized form (**17** or **8**) [Eq (7)]. Alternatively, the living polymer **16** may be further utilized to polymerize another monomer to give tri-armed block copolymers (**9**). In cationic polymerization, the synthesis of tri-armed polymers by this method has extensively been investigated by Kennedy's group for isobutene[11] but none for other vinyl monomers.



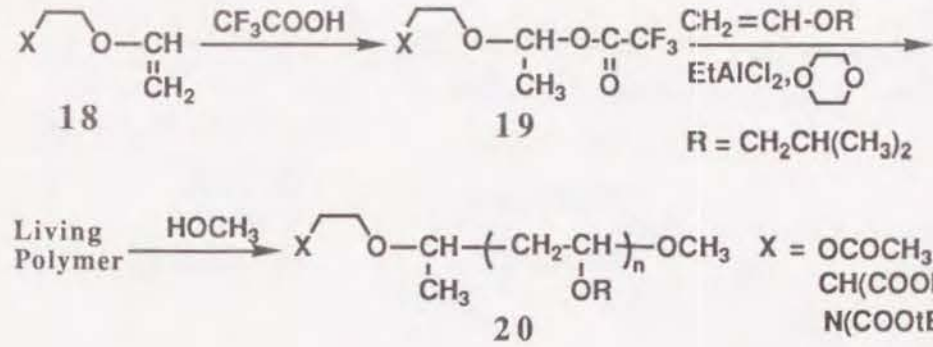
(7)

In this study, the author examined the synthesis of tri-armed end-functional polymers (**8**) and tri-armed block polymers (**9**) on the basis of trifunctional initiators (**15**) [Eq (7)]. To this end, a series of new trifunctional initiators for living cationic polymerization were designed and prepared.

Outline of This Study

Based on the considerations given above, the present thesis deals with the synthesis of telechelic polymers and tri-armed functional polymers by living cationic polymerization. ***Part 1*** concerns telechelic polymers of vinyl ethers (Chapters 1 and 2) and *p*-alkoxystyrenes (Chapters 3 and 4).

Chapter 1 describes a survey of initiators for the "*functional initiator method*" [Eq (4)] in cationic polymerization of isobutyl vinyl ether (IBVE), which in turn led to a basis of the synthesis of telechelic polymers via living cationic polymerization to be described in the following chapters.

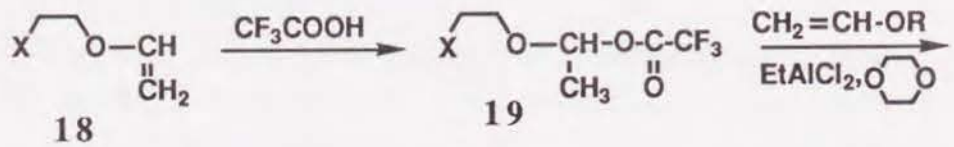


(8)

More specifically, as functional initiators were empolyed herein a series of trifluoroacetates (**19**) that were obtained by addition of trifluoroacetic acid to a vinyl ether (**18**) with a funcional pendant group (X) [Eq (8)]; X is such that is a protected form of a hydroxy, carboxy, or amino function. The initiator **19** was coupled with ethylaluminum dichloride ($EtAlCl_2$) as an activator and with an excess of 1,4-

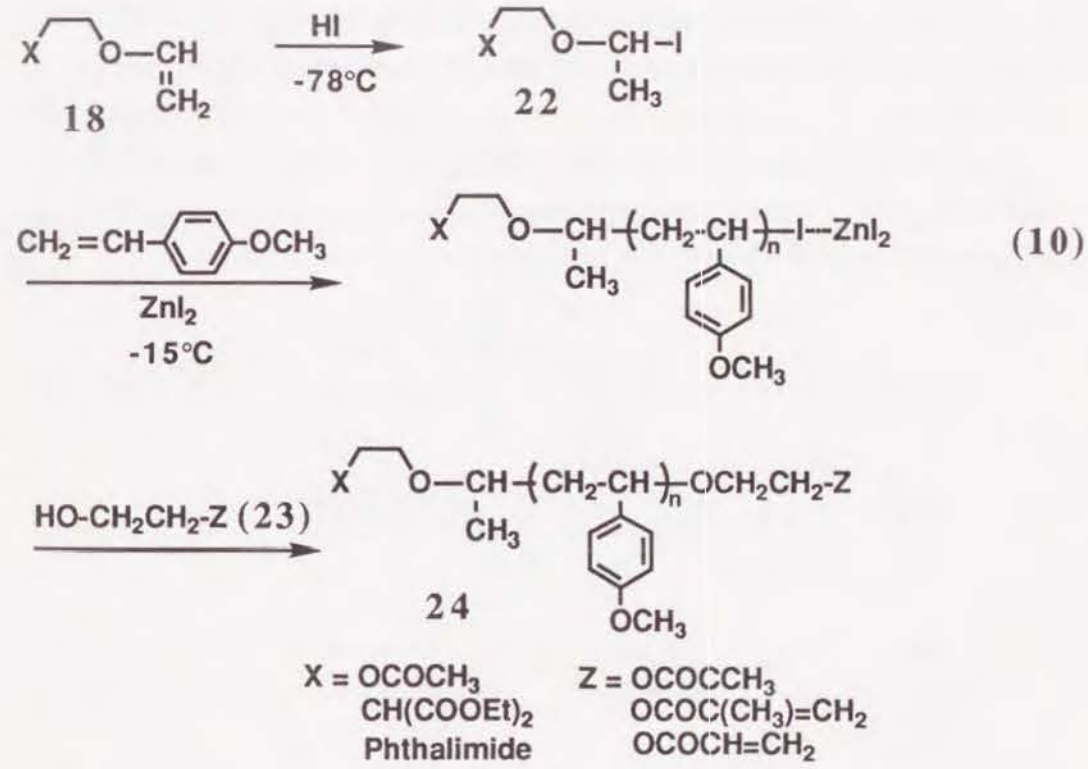
dioxane as an added base for cation stabilization (see above). These initiating systems invariably induced a well-defined living polymerization of IBVE at relatively high temperatures (up to +40°C) to give polymers (**20**), the α-end group (X) of which was derived from **19.** Subsequent deprotection of X of these polymers led to hydroxy, carboxy, or amino-capped poly(IBVE) quantitatively.

Chapter 2 presents a survey directed to end-capping agents for the "*end-capping method*" [Eq (6)], which is another basis of the telechelic polymer synthesis. The survey established that one of the best end-capping agents for vinyl ether is the sodium salt of ethyl malonate in the living cationic polymerization based on added bases. This end-capping method was then combined with the functional initiator method discussed in Chapter 1 and, as shown in Eq (9), a series of *hetero*- and *homo*-telechelic poly(IBVE) (**21**) were synthesized at a relatively high temperature (+60°C).

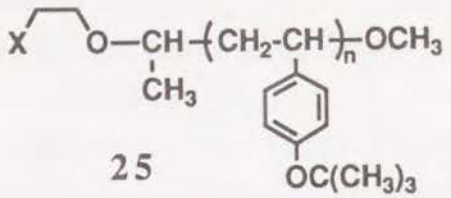


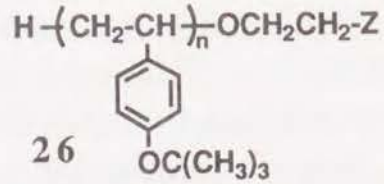
Chapter 3 is focused on the initiators and end-capping agents suited for *p*-alkoxystyrenes. In contrast to vinyl ethers (Chapters 1 and 2), *p*-alkoxystyrenes required living polymerization based on nucleophilic counteranions (the iodide anion) rather than added bases. Thus, as summarized in Eq (10), the adduct (**22**)

of hydrogen iodide with a pendant-functionalized vinyl ether (**18**) was found to initiate living cationic polymerization of *p*-methoxystyrene (pMOS) in the presence of zinc iodide (ZnI_2) as an activator. Also, compared with vinyl ethers, a wider variety of end-capping agents such as alcohols (**23**) proved applicable for *p*-alkoxystyrenes. With these initiators and end-capping agents, a series of telechelic poly(pMOS) **24** were subsequently synthesized [Eq (10)], where typical examples include *hetero*-telechelic poly(pMOS) macromonomers with OH (X) and $OCOC(CH_3)=CH_2$ (Z).



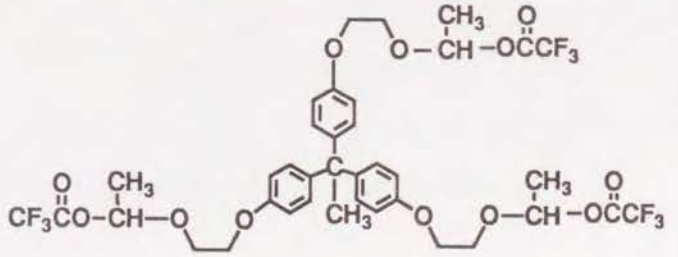
Chapter 4 illustrates the synthesis of end-functionalized polymers of *p-t*-butoxystyrene (tBOS), which is of interest as a precursor of poly(*p*-hydroxystyrene). In a similar manner to pMOS (Chapter 3), a series of end-functionalized poly(tBOS) with α-end (**25**) or ω-end (**26**) functions were synthesized.





Part 2 of this thesis concerns the synthesis of tri-armed functional polymers where arms are end-functionalized (**8**; Chapters 5 and 7) or amphiphilic block segments (**9**; Chapter 6) of vinyl ethers and *p*-alkoxystyrenes.

Chapter 5 focuses on the first synthesis of tri-armed polymers of vinyl ethers [Eq (11)]. For this, new trifunctional initiators like **27** were prepared from the corresponding trifunctional vinyl ethers and trifluoroacetatic acid.



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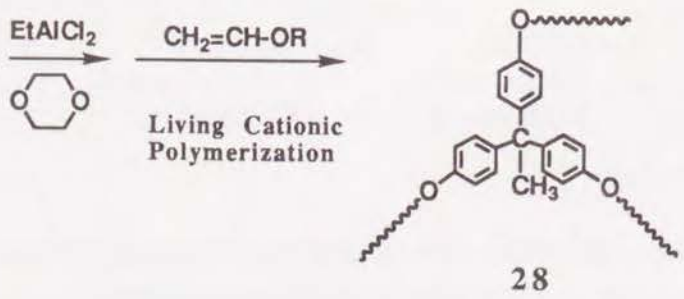
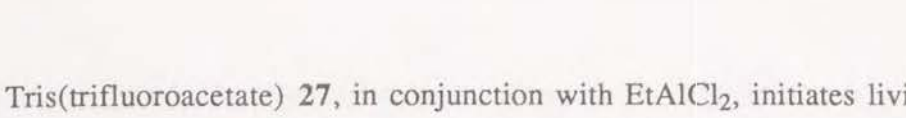
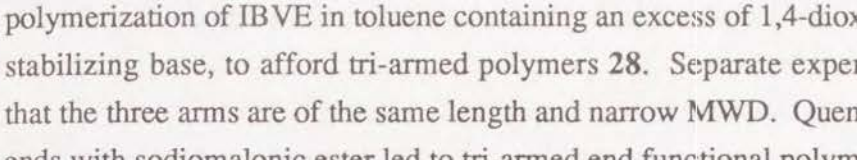


Tris(trifluoroacetate) **27**, in conjunction with $EtAlCl_2$, initiates living cationic polymerization of IBVE in toluene containing an excess of 1,4-dioxane as a cation-stabilizing base, to afford tri-armed polymers **28**. Separate experiments verified that the three arms are of the same length and narrow MWD. Quenching the living ends with sodiomalonic ester led to tri-armed end functional polymers capped with carboxylic acids.

Chapter 6 deals with the synthesis of tri-armed amphiphilic block polymers [Eq (12)]. The **27**/$EtAlCl_2$ initiating system is also applicable to vinyl ethers with functional pendant group (e.g., CH_2=CH-OCH_2CH_2-$OCOCH_3$; AcOVE). Thus, sequential polymerization of IBVE and AcOVE, initiated with the **27**/$EtAlCl_2$ system in the presence of excess 1,4-dioxane, afforded tri-armed block copolymers (**29**) that, upon hydrolysis of the pendant acetates into hydroxyl groups, can be converted into tri-armed polymers consisting of a hydrophobic poly(IBVE) segment and a hydrophilic polyalcohol segment





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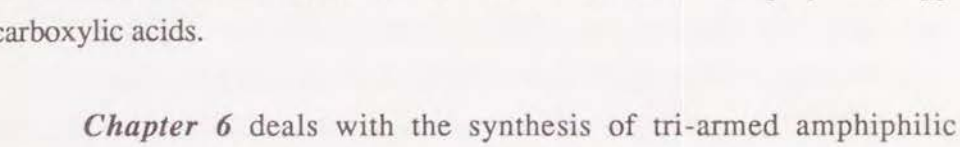
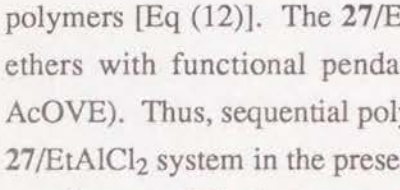
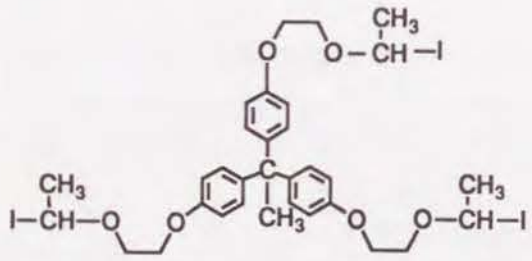




	R¹ (Inner)	R² (Outer)
29a	$CH_2CH(CH_3)_2$	$CH_2CH_2OCOCH_3$
29b	$CH_2CH_2OCOCH_3$	$CH_2CH(CH_3)_2$

$\mathrm{+CH_2CH(OCH_2CH_2OH)+_n}$. By altering the polymerization sequence of IBVE and AcOVE, the hydrophilic segments (▬) can be placed either outside (**29a**) or inside (**29b**).

Chapter 7 discusses the synthesis of tri-armed polymers of pMOS via living cationic polymerization with a trifunctional vinyl ether-hydrogen iodide adduct (**30**) in conjunction with ZnI_2 at -15°C. This initiating system gave tri-armed poly(pMOS) where the three arm chains possessed nearly the same and uniform lengths. End-capping of the living ends with alcohols (e.q., 2-hydroxyethyl methacrylate) gave tri-armed end functional poly(pMOS), including tri-armed methacrylate-type macromonomers.



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In conclusion, the present study has achieved the synthesis of a wide variety of telechelic polymers and tri-armed functional polymers of vinyl ethers and *p*-alkoxystyrenes. The auther hopes that this study will contribute toward extending the scope of living polymerization into the synthesis of novel advanced polymer materials.

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PART 1

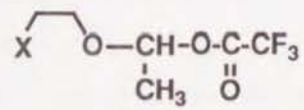
SYNTHESIS OF TELECHELIC POLYMERS BY LIVING CATIONIC POLYMERIZATION

CHAPTER 1

END-FUNCTIONALIZED POLYMERS OF ISOBUTYL VINYL ETHER

ABSTRACT

A series of end-functionalized polymers (**4**), carrying a hydroxyl, carboxyl, or primary amino terminal group Y, were obtained by living cationic polymerization of isobutyl vinyl ether. The initiating systems of choice consisted of $EtAlCl_2$ and the trifluoroacetate [**2**; X-$CH_2CH_2OCH(CH_3)OOCCF_3$; X = $OOCCH_3$, $CH(COOC_2H_5)_2$, $N(COOC(CH_3)_3)_2$] obtained from a vinyl ether with a protected functional pendant group. In the presence of 1,4-dioxane, the **2**/$EtAlCl_2$ systems invariably induced a well-defined living polymerization of isobutyl vinyl ether in *n*-hexane at 0°C to +40°C to give polymers, the α-end group (X) of which was derived from the initiator **2**. Subsequent deprotection of X of these polymers led to **4**, all of which were shown to have a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.07-1.18), a number-average molecular weight ($\bar{M}_n$ = 10^3-10^4) controllable by the monomer/**2** feed molar ratio, and one terminal function Y per chain.



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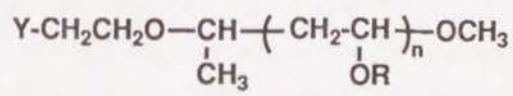
X = $OCOCH_3$ (2a),
$CH(COOEt)_2$ (2b),
$N(COOtBu)_2$ (2c)



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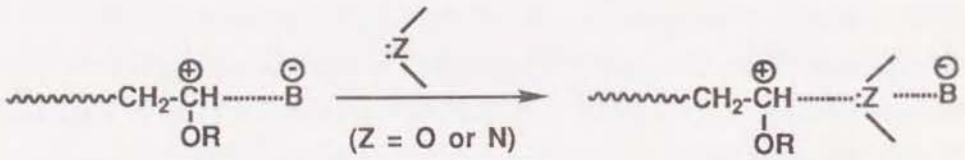
Y = OH (4a), CH_2COOH (4b), NH_2 (4c)
R = $CH_2CH(CH_3)_2$

INTRODUCTION

Living cationic polymerization of vinyl ethers has been shown to occur with ethylaluminum dichloride ($EtAlCl_2$) in the presence of an externally added weak base,[1] including an ester[2] and ether.[3] The added base (:Z) is proposed to stabilize the otherwise unstable growing carbocation by cationic charge delocalization through a strong nucleophilic interaction, as shown in Scheme I where $B^{\ominus}$ is the counteranion derived from $EtAlCl_2$.

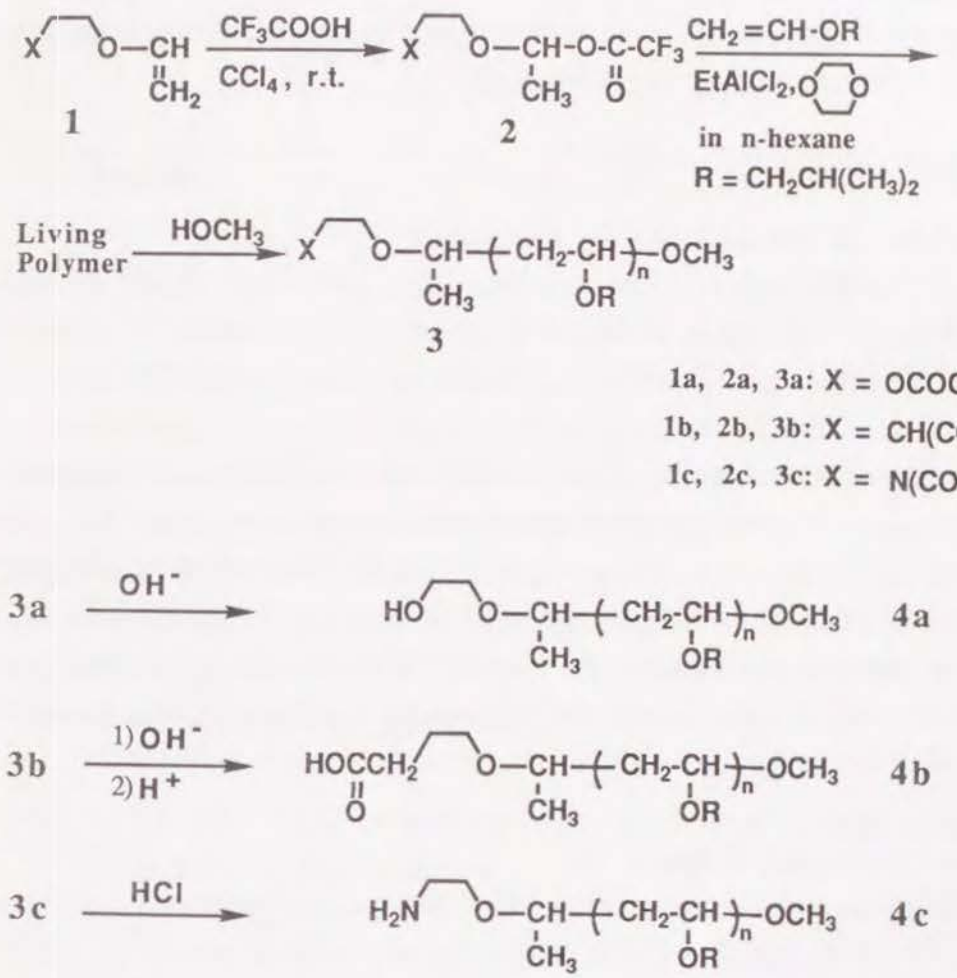


Not Living **Living**

Scheme I. Carbocation Stabilization by an Added Base.

In addition of an added base, the $EtAlCl_2$-mediated living polymerization usually employs a cationogen (or initiator), typically an acetate CH_3COOY, that generates an initiating cation ($Y^{\oplus}$) with aid of the organoaluminum.[2] We have shown the formation of one living chain per molecule of the cationogen, which fact in turn implies the attachment of the initiator fragment Y to each polymer terminal. It readily follows (Scheme II) that the use of similar but functionalized initiators **2**, obtained from a vinyl ether **1**, will lead to polymers **3** with a terminal function X. The object of this study to be described in this chapter was to synthesize end-functionalized poly(vinyl ethers) **4** in a controlled manner on the basis of this methodology.

The synthesis route illustrated in Scheme II is similar to our a known method[4-6] using a hydrogen iodide adduct of a functionalized vinyl ether as an initiator and iodine as an activator, in that the terminal functionality is derived from the initiator. However, the use of **2**/$EtAlCl_2$ is unpreceded in concept, because the living polymerization initiated by this system is based on the carbocation stabilization by an added base (Scheme I), whereas that with the hydrogen iodide adduct utilizes the nucleophilic iodide counteranion for stabilizing the growing cation.[1]



Scheme II Synthesis of End-Functionalized Polymers 4 with $EtAlCl_2$

The author herein discusses the synthesis of a series of end-functionalized polymers **4** carring a terminal hydroxyl (**4a**), carboxyl (**4b**), or primary amino (**4c**) group, according to Scheme II that consists of the living cationic polymerization of isobutyl vinyl ether (IBVE) initiated by the **2**/$EtAlCl_2$ system in *n*-hexane in the presence of 1,4-dioxane as an added base, followed by deprotection of the terminal group X of the precursor polymer **3** (Eq. 1-3).

RESULTS AND DISCUSSION

1. Synthesis of Trifluoroacetate Initiator 2

Despite the frequent use of vinyl ether-acetic acid adducts as the initiators for the living polymerization with $EtAlCl_2$ and an added base,[1] the author decided in this study to replace them with the corresponding trifluoroacetates (**2**). It turned out that the reaction of the functionalized vinyl ethers **1** into **2** is invariably quantitative with trifluoroacetic acid but not with acetic acid; in contrast, the addition of acetic acid to nonpolar alkyl vinyl ethers is quantitative. Thus, the trifluoroacetate initiators **2** were prepared by mixing **1** with an equimolar amount of CF_3COOH in CCl_4 at room temperature under dry nitrogen.[7] After its quantitative formation had been confirmed by ^1H and ^{13}C NMR spectroscopy, the resulting solution of **2** was directly employed for the subsequent living polymerization of IBVE.

2. Hydroxy-Capped Polymer 4a

IBVE was polymerized at 0 and +40 °C in *n*-hexane containing 1,4-dioxane (1.2 M; 10 vol %) with $EtAlCl_2$ in conjunction with trifluoroacetate **2a**, which carries an acetate pendant group as a protected form of a hydroxyl function. The $EtAlCl_2$/**2a** feed ratio was set in the range 0.50 - 1.0, on the basis of preliminary experiments carried out at various $EtAlCl_2$ concentrations. As summarized in Table I (entry 1 and 2), the polymerization quantitatively gave living polymers with very narrow molecular weight distributions (MWD) ($\bar{M}_w/\bar{M}_n < 1.1$).

Table I

Synthesis of Polymer **3** by the Living Cationic Polymerization of IBVE with **2**/$EtAlCl_2$ in *n*-Hexane in the Presence of 1,4-Dioxane[a]

Entry	X	$\frac{[EtAlCl2]_0}{[2]_0}$	Temp °C	$\overline{DP}_n$[b] (calcd)	$\overline{DP}_n$[c] (obd)	$\frac{\bar{M}_w}{\bar{M}_n}$[e]	$\overline{F}_n(A)$[d,f]	$\overline{F}_n(B)$[d,g]
1	$OOCCH_3$	1.0	0	19.0	18.0	1.07	1.06	1.00
2	$OOCCH_3$	0.50	+40	19.0	19.1	1.13	1.02	1.02
3	$CH(COOEt)_2$	0.80	0	14.7	14.5	1.14	1.02	1.01
4	$CH(COOEt)_2$	0.50	+40	19.0	20.2	1.18	1.09	1.03
5	$N(COOtBu)_2$	4.0	0	10.0	9.9	1.13	0.96	0.95

a) $[IBVE]_0$ = 0.38 M (5.0 vol%); $[2]_0$ = 20–40 mM; [1,4-dioxane] = 1.2 M (10 vol%); conversion ca. 100 % by gas chromatography.

b) $\overline{DP}_n(calcd) = [IBVE]_0/[2]_0$.

c) $\overline{DP}_n(obd) = [IBVE]_0/[P^*]$; [P*] represents the living end concentration determined from the peak intensity of the acetal terminal; see text.

d) Measured by ^1H NMR spectroscopy.

e) Measured by size-exclusion chromatography with a polystyrene calibration.

f) $\overline{F}_n(A) = [X]/[2]_0$; [X] represents the concentration of the terminal functional group X derived from **2**; see text.

g) $\overline{F}_n(B) = [X]/[P^*]$.

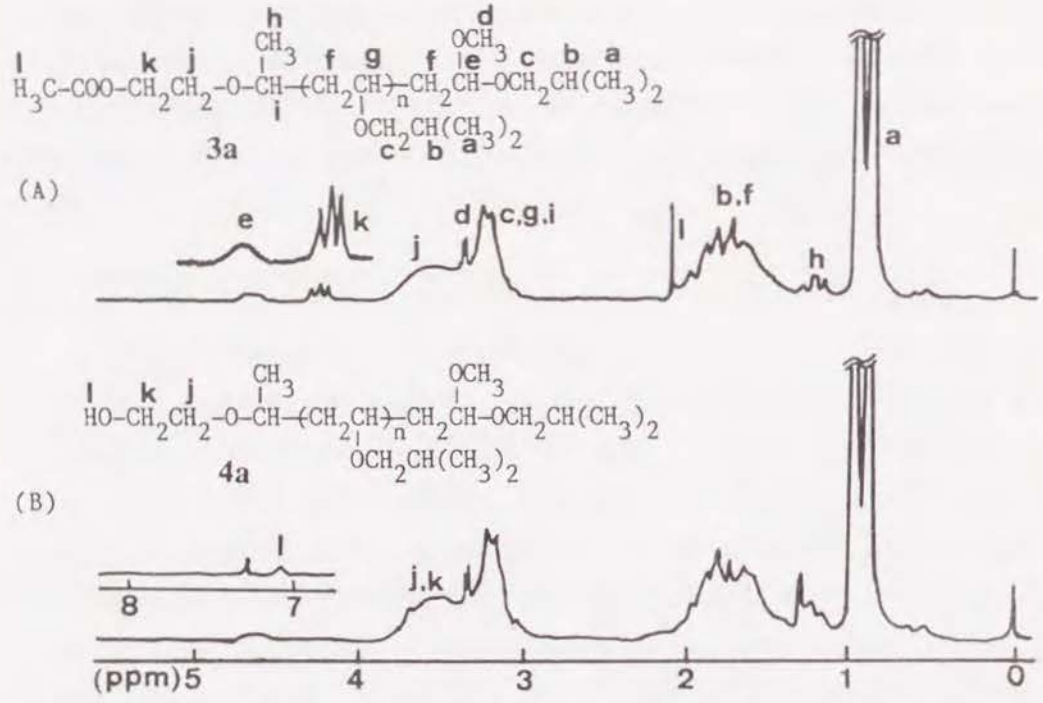


Figure 1. ^{1}H NMR spectra (90 MHz, $CDCl_3$):
(A) acetate-capped poly(IBVE) **3a** (sample 1, Table I);
(B) hydroxy-capped poly(IBVE) **4a** obtained from sample 1.

Figure 1A shows the ^{1}H NMR spectrum of a typical product (sample 1, Table I), along with peak assignment. All key absorptions of the poly(IBVE) main-chain (a, b, c, f, and g) and the initiator fragment (α-end; h, k, and l) are seen, all of which are consistent with the expected structure of polymer **3a**. The additional signals d and e are due to the acetal terminal [ω-end; $CH_2CH(iBu)OCH_3$] that arises from quenching the living end with ammoniacal methanol.[4]

Comparison of the integrated intensities of these key resonances confirmed the clean and quantitative formation of **3a** (Table I). For example, the concentration ([X]) of the α-end group X, determined from peak k or l and peak a [CH_3 of the poly(IBVE) chain], was shown to be equal to the initial concentration of the initiator **2a** ($\overline{F}_n(A) = [X]/[\mathbf{2a}]_0 = 1$). [X] was also found equal to the living end

concentration [P^*] based on the acetal terminal e ($\overline{F}_n(B) = [X]/[P^*] = 1$); i.e., the signal intensity ratio of e/k was very close to the expected value (1/2). In addition, the number-average degree of polymerization, $\overline{DP}_n$(obd), which was determined from the ratio of the main-chain and the terminal acetal protons (a/e), was in agreement with the calculated value ($\overline{DP}_n(calcd) = [IBVE]_0/[\mathbf{2a}]_0$).

All these data show the IBVE polymerization by **2a**/$EtAlCl_2$ in the presence of 1,4-dioxane to produce well-defined polymer **3a** which has one terminal function X per chain and a controlled molecular weight. It should be emphasized that the synthesis operates even at +40°C, at which temperature the corresponding process using the hydrogen iodide adduct has not proved successful yet.[4-6]

The terminal acetate group of **3a** was turned out to be readily converted into a hydroxyl function (**4a**) by the standard alkaline hydrolysis in ethanol at room temperature [Eq (1), Scheme II];[6,8] a typical example of the ^{1}H NMR spectrum of the hydrolysis product is given in Figure 1B. The signals associated with the acetate terminal of **3a** (peak k and l, Figure 1A) are absent in Figure 1B, where the alcoholic proton of **4a** is in turn seen around δ 7.1 ppm.

3. Carboxy-Capped Polymer 4b

In a fashion similar to the above, the carboxyl version **4b** was prepared from vinyl ether **1b** via the precursor **3b** (Scheme II). Thus, the polymerization of IBVE by the **2b**/$EtAlCl_2$ system was carried out in *n*-hexane in the presence of 1,4-dioxane, which again gave living polymers of narrow MWDs in quantitative yield both at 0 and +40°C (Table I, entry 3 and 4). The ^{1}H NMR spectrum of the product (Figure 2A) is fully consistent with the structure **3b**, as evidenced by signals h, k, m, and n for the malonate group and d and e for the acetal terminal. Quantitative attachment of the malonate function to the polymer's α-end was shown by comparing the peak intensity ratios (see Table I); $\overline{DP}_n$(obd) of **3b** also proved controllable by the IBVE/**2b** molar feed ratio.

As shown in Figure 2B, the malonate terminal of **3b** could readily be transformed into the corresponding carboxylic acid (**4b**) by alkaline hydrolysis in ethanol at room temperature, followd by thermal decarboxylation in 1,4-dioxane at 90°C [Eq (2), Scheme II].[6] The quantitative deprotection is shown, for example,

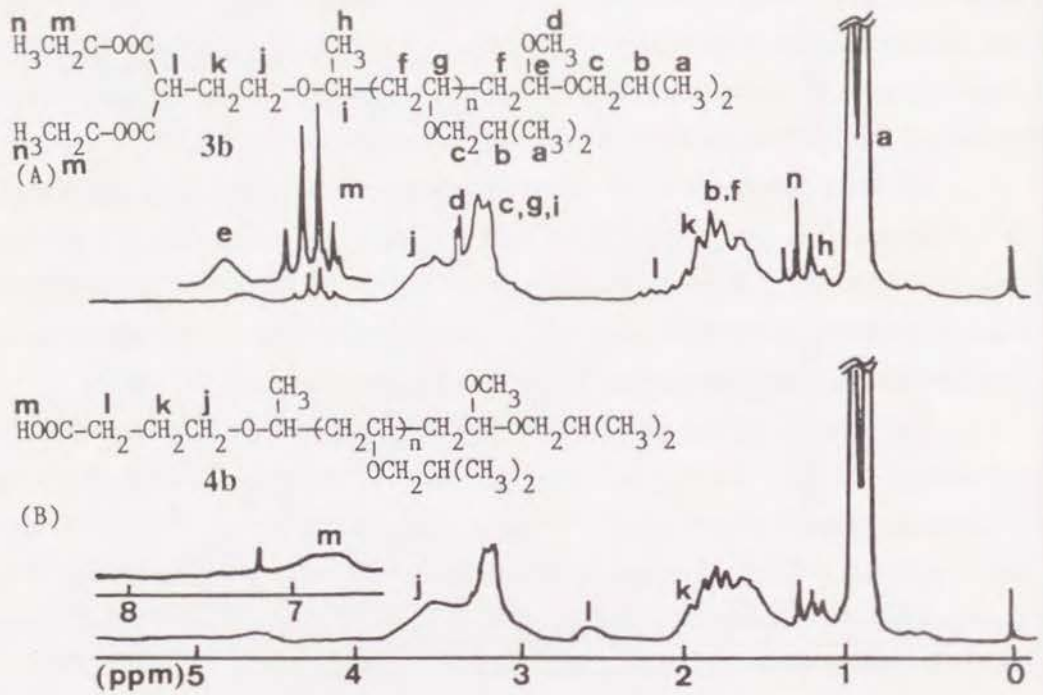


Figure 2. ^{1}H NMR spectra (90 MHz, $CDCl_3$):
(A) malonate-capped poly(IBVE) **3b** (sample 3, Table I);
(B) carboxy-capped poly(IBVE) **4b** obtained from sample 3.

by the complete disappearance of the ester's ethyl groups (peaks m and n; cf. Figure 2A), coupled with the observation of the acid proton as a broad signal m in Figure 2B.

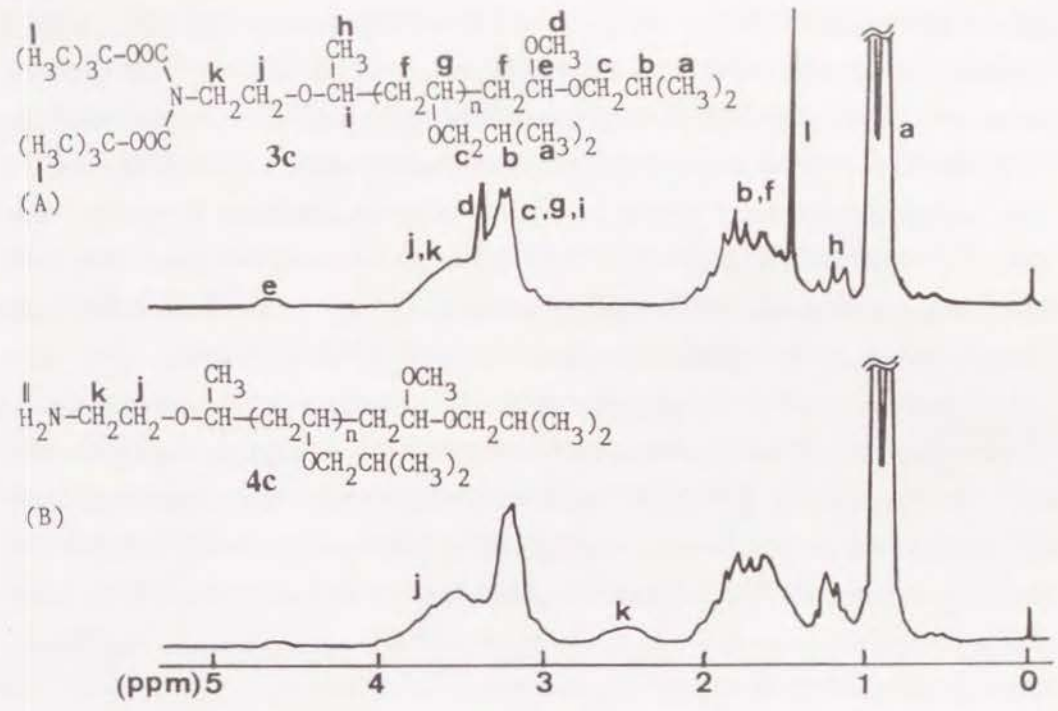


Figure 3. ^{1}H NMR spectra (90 MHz, $CDCl_3$):
(A) imide-capped poly(IBVE) **3c** (sample 5, Table I);
(B) amine-capped poly(IBVE) **4c** obtained from sample 5.

4. Amine-Capped Polymer 4c

Higashimura et al.[9] have successfully employed 2-(vinyloxy)-ethylphthalimide, as a vinyl ether with a protected amino group, for living cationic polymerization. It soon turned out, however, that the reaction of this monomer with CF_3COOH does not quantitatively proceed in CCl_4 at room temperature. Thus, the author newly synthesized *N*-[2-(vinyloxy)ethyl]di-*t*-butylcarboxyimide (**1c**), another protected form of an amino-functionalized vinyl ether, for which addition of CF_3COOH now proved quantitative under the same conditions to give **2c**.

In the presence of $EtAlCl_2$ and 1,4-dioxane, the initiator **2c** induced living polymerization of IBVE in *n*-hexane at 0°C to form polymers (**3c**) with a narrow MWD and a controlled molecular weight (Table I, entry 5). The ^1H NMR spectrum of the product (Figure 3A) clearly showed the quantitative incorporation of the imide function of **2c** into the polymer terminal (e.g., peak 1 for the *t*-butyl moiety). This signal, though very sharp, could not fully be resolved from the broad absorption appearing around δ 1.3-2.1 ppm, so that the concentration of the imide function was determined by comparing the intensity ratio of the latter broad band (including peak 1) to another broad absorption in the range δ 3-4 ppm.

Deprotection of the imide group in the precursor **3c** was carried out in nitromethane at room temperature in the presence of a few drops of concentrated hydrochloric acid (Eq. 3, Scheme II).[10] ^1H NMR analysis of the product (Figure 3B) again showed quantitative conversion of the imide group into a primary amino function (or polymer **4c**). For example, the imide's sharp signal 1 (cf. Figure 3A) is now completely absent, whereas the methylene protons adjacent to the primary amino group are seen as a broad signal around δ 2.5 ppm.

In conclusion, the synthesis of end-functionalized poly(IBVE) **4** has been shown to be feasible, not only via living cationic polymerization by the hydrogen iodide-based initiating system (based on the carbocation stabilization with a nucleophilic counteranion)[4-6] but also via the similar process by the **2**/$EtAlCl_2$ system (via the carbocation stabilization with an added base; Scheme II), where the latter is advantageous in that it operates even above room temperature.

EXPERIMENTAL

Preparation of Functionalized Vinyl Ethers (1).

2-Acetoxyethyl vinyl ether (**1a**)[8] and diethyl 2-vinyloxyethyl malonate (**1b**)[6] were prepared according to the literature methods.

Di-*t*-butyl *N*-[2-(vinyloxy)ethyl]imidedicarboxylate (**1c**) was prepared as follows. In a 300 mL, three-necked, round-bottom flask fitted with a magnetic stirrer, a reflux condenser, and a dropping funnel were charged di-*t*-butyl iminodicarboxylate, $HN[CO_2C(CH_3)_3]_2$ (10.0 g, 46 mmol) (Aldrich, purity 95%), sodium hydroxide aqueous solution (1 M, 43 mL, 43 mmoL NaOH), and dimethyl sulfoxide (100 mL). After stirred for 1 h at room temperature, the reaction mixture was then warmed to 80°C in an oil bath, and 2-chloroethyl vinyl ether (9.2 g, 92 mmoL) and tetra-*n*-butylammonium bromide (1 g; a phase-transfer catalyst) were added. The heterogeneous solution was stirred at this temperature for 6 h, cooled to room temperature, and then poured into 500 mL of water. The aqueous phase was extracted with three 50-mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed twice with water (100 mL each) and evaporated under reduced pressure to give a yellowish viscous liquid. The crude product was purified by preparative size-exclusion chromatography (column: Shodex 2001 polystyrene gel; solvent: $CHCl_3$); the collected fractions in chloroform was dried with sodium sulfate overnight and evaporated to dryness under reduced pressure to give **1c** as a light yellowish viscous liquid: yield, 60 %; purity > 98 % by ^1H NMR; ^1H NMR ($CDCl_3$): δ 6.44 (q, 1H, =CH-), 4.11 (m, 2H, CH_2=), 3.86 (t, 4H, -CH_2CH_2-), 1.50 (s, 18H, C-CH_3); ^{13}C NMR ($CDCl_3$): δ 152.4 (C=O), 151.4 (=CH), 86.7 (CH_2=), 82.2 (-C-), 66.0 (O-CH_2), 44.9 (CH_2-N), 27.9 (C-CH_3).

Other Materials

The monomer (IBVE), solvent (*n*-hexane), 1,4-dioxane, and $EtAlCl_2$ were purified as reported.[2,3] Polymerization by **2**/$EtAlCl_2$ was carried out under dry nitrogen in a baked glass tube equipped with a three-way stop-cock. The reaction was initiated by sequential addition of solutions of **2** and $EtAlCl_2$ into a mixture of IBVE and 1,4-dioxane in *n*-hexane, and quenched with ammoniacal methanol.

Procedures

Polymerization was performed under dry nitrogen in baked glass tubes each equipped with a three-way stopcock. The reactions were initiated by sequencial addition of the initiator **2** and $EtAlCl_2$ solutions (0.50 mL each) into a monomer solution (4.0 mL in *n*-hexane) containing 1,4-dioxane (0.50 mL, 1.2 M, 10 vol%) at 0 or +60°C. The resulting living polymers were terminated with solutions of a capping agent (see Table I), which was 10-fold molar excess over the initiator (**2**).

Polymer Characterization

The MWD of the polymers was measured by size-exclusion chromatography in chloroform at room temperature on Jasco Trirotor chromatograph equipped with three polystyrene gel columns (Shodex; exclusion limits: K-802, 5×10^3; K-803, 7×10^4; K-804, 4×10^5) that were calibrated against 12 standard polystyrene samples. The $\bar{M}_w/\bar{M}_n$ of the polymers were calculated from size-exclusion eluograms. ^{1}H NMR spectra were recorded at 270 MHz in $CDCl_3$ at room temperature on a Jeol GSX-270 spectrometer. $\overline{DP}_n$ was determined by ^{1}H NMR end-group analysis (see Results and Discussion).

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CHAPTER 2

HOMO- AND HETERO-TELECHELIC POLYMERS OF ISOBUTYL VINYL ETHER

ABSTRACT

A series of hetero- and homo-telechelic polymers (**3** and **8**) of isobutyl vinyl ether (IBVE) were synthesized via living cationic polymerization at a relatively high temperature:

X-CH_2CH_2O-$CH(CH_3)$-$(CH_2CH(OiBu))_n$-$CH(COOC_2H_5)_2$ (**3**)
(X: $OOCCH_3$ (**3a**), $N[COOC(CH_3)_3]_2$ (**3b**), $CH(COOC_2H_5)_2$ (**3c**))

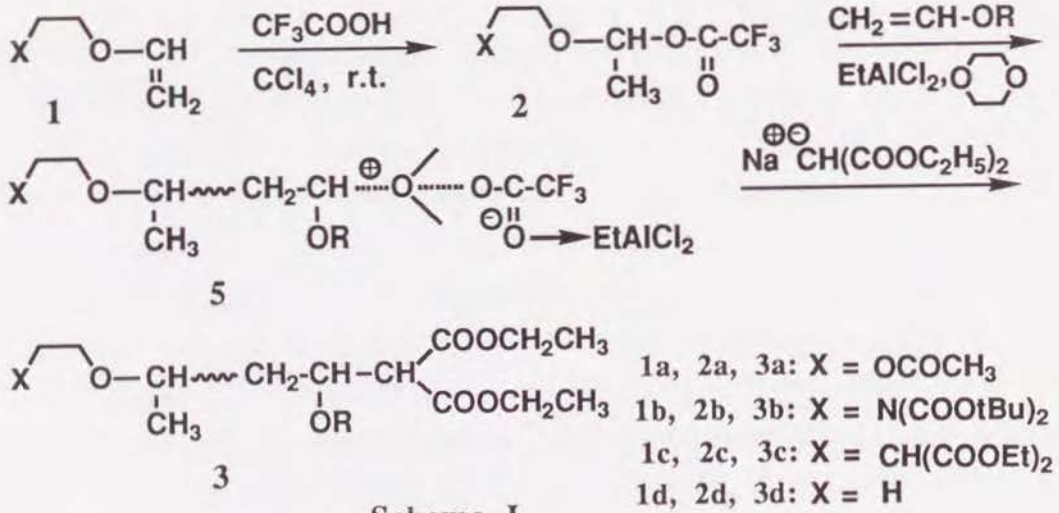
X-CH_2CH_2O-$CH(CH_3)$-$(CH_2CH(OiBu))_n$-C_6H_5 (**8**)
(X: $CH(COOC_2H_5)_2$).

The α-end function X was introduced by use of initiating systems where functional trifluoroacetate initiators (**2**; X-$CH_2CH_2OCH(CH_3)OOCCF_3$), obtained from vinyl ether X-$CH_2CHOCH{=}CH_2$, were coupled with $EtAlCl_2$ (activator) and excess 1,4-dioxane (carbocation stabilizer) in *n*-hexane solvent at 0 and +60°C. The ω-end functions included malonate and phenyl groups that were introduced by end-capping the resulting living ends with sodiomalonic ester [$NaCH(COOC_2H_5)_2$] and phenyllithium, respectively. Structural analysis of the products, even obtained at +60°C, corroborated their controlled molecular weights ($\overline{DP}_n = [IBVE]_0/[\mathbf{2}]_0$; $\bar{M}_w/\bar{M}_n < 1.1$) and the attachment of two terminal functions per polymer except for the imide derivative **3b**, for which the end-functionality was lower (~60 %) at +60°C. Telechelic polymers **3** could be converted into **4**, with a hydroxy, amino, or carboxy group at the α-end (Y) and with a carboxy group at the ω-end:

Y-CH_2CH_2O-$CH(CH_3)$-$(CH_2CH(OiBu))_n$-CH_2COOH (**4**)
(Y: OH, NH_2, CH_2COOH)

INTRODUCTION

Telechelic polymers, indispensable building blocks for advanced polymeric materials, may be prepared by a variety of methods, among which living polymerization is most effective in controlling their molecular weight and end functionality.[1,2] In a typical synthesis of telechelic polymers, living polymerization is initiated by a bifunctional initiator, and the resulting diheaded living active sites are end-capped with a reagent having a functional group. Although this method is simple to operate, it can afford, by definition, only telechelics that carry the same terminal functions (homo-telechelic polymers; X~~~X). In another approach, living polymerization is initiated by an initiator with a functional group (X), followed by quenching the monofunctional living end with a capping agent with another functional group (Y). This method can provide not only homo-telechelic polymers (X = Y) but also so-called "hetero-telechelic" polymers (X~~~Y; X = Y), where the two terminal functions differ from each other.



Scheme I

As discussed in Chapter 1,[3] terminally monofunctional polymers (**5**) of vinyl ethers can be synthesized by living cationic polymerization that is initiated

with a functional initiator (**2**) obtained from a vinyl ether (**1**) with a pendant function X. The living process (Scheme I) is carried out in the presence of ethylaluminum dichloride ($EtAlCl_2$) and a stoichiometric excess of 1,4-dioxane, which are, respectively, an activator for the initiator **2** and a Lewis base for stabilization of the growing carbocation.[4,5] From isobutyl vinyl ether (IBVE), for example, this method affords polymers that carry a "head" functional group X derived from the initiator **2**.

The study described in this chapter was to extend this methodology to the controlled synthesis of homo- and hetero-telechelic polymers at relatively high temperature up to +60°C (Scheme I). To this end, the head-functionalized living polymer **5** was quenched with a variety of functional nucleophiles so as to attach a "tail" (ω-end) function. Scheme I illustrates examples of such syntheses where sodiomalonic ester[6,7] is employed as capping agent to give telechelic polymers **3a** – **3c**, which can be converted into more versatile forms [**4a** – **4c**, respectively; Eq. (1) – (3)] with combinations of hydroxy, amino and carboxy functions. Phenyllithium was also found to be a new end-capping agent that leads to an ω-end phenyl group. Among the reported examples of telechelic polymers of vinyl compounds via living cationic polymerization,[1] there are few of hetero-telechelic polymers.[2]

RESULTS AND DISCUSSION

1. Survey of End-Capping Agents

As discussed already,[2] the **2**/$EtAlCl_2$ initiating system permits truly living cationic polymerization of vinyl ethers. For the synthesis of telechelic polymers via the general route illustrated in Scheme I, the author first surveyed end-capping agents that combine quantitatively with the living end (**5**) without inducing β-proton elimination. Except for sodiomalonic ester,[6,7] it remains unknown which types of nucleophiles are suited for such selective end-capping agents for the living species **5**, which is stabilized by an externally added Lewis base (1,4-dioxane) but still involves labile β-protons.

Table I summerizes the results of end-capping experiments with use of six carbanion salts, among which compounds **6** and **7** are lithium salts of protected

Table I

End-Capping Reactions of Living Poly(IBVE) with Various Carbanions[a]

Capping Agent[b]	End Group	$\overline{F}_n$[c]
$Li(CH_2)_3CH_3$	$-(CH_2)_3CH_3$	0
$Li(CH_2)_3OCH(CH_3)OC_2H_5$ (**6**)	$-(CH_2)_3OCH(CH_3)OC_2H_5$	0
$Li(CH_2)_2OSi(CH_3)_3$ (**7**)	$-(CH_2)_2OSi(CH_3)_3$	0
LiC_6H_5	$-C_6H_5$	1.01
$BrMgC_6H_5$	$-C_6H_5$	1.00
$NaCH(COOC_2H_5)_2$	$-CH(COOC_2H_5)_2$	1.01
		1.00[d]

a) Polymerization by **2d**/$EtAlCl_2$ in *n*-hexane at 0°C; $[IBVE]_0$ = 0.38 M; $[\mathbf{2d}]_0$ = $[EtAlCl_2]_0$ = 20 mM; [1,4-dioxane] = 1.2 M; conversion~100 % in 15 min; [capping Agent] = 200 mM.

b) Added as solution in: $Li(CH_2)_3CH_3$, *n*-hexane; **6** and **7**, tetrahydrofuran; LiC_6H_5, cyclohexane/diethyl ether (7/3, v/v); $BrMgC_6H_5$, tetrahydrofuran; $NaCH(COOC_2H_5)_2$, 1,4-dioxane. For all runs, the reaction of capping agent with the living end was for 60 min.

c) $\overline{F}_n$ = [end group]/$[\mathbf{2d}]_0$ by ^1H NMR; see text.

d) Polymerization at +60°C.

alcohols.[8] Despite the frequent use for termination of cationic polymerization, alcohols[6,9,10] and amines[11,12] were excluded from the screening, because, specifically when employed to vinyl ethers, these oxygen and nitrogen bases would lead to acetal and aminoether terminals, respectively, which are not very stable under acidic conditions at high temperature. For simplicity, the polymerization for the search of end-capping agents was initiated with a non-functionalized initiator **2d** (X : H), which was derived from ethyl vinyl ether, coupled with $EtAlCl_2$ activator in *n*-hexane at 0 or +60°C in the presence of excess 1,4-dioxane (1.2 M, 10 vol%).

Under these conditions, the polymerization was living ([living end] = $[\mathbf{2d}]_0$)[2] and reached > 95% conversion, at which moment end-capping agents were added (10-fold molar excess over the living end **5**).

The three primary alkyllithium compounds [*n*-butyllithium (BuLi), **6**, and **7**] turned out totally ineffective as capping agents. Though treated with a large excess of these salts, no alkyl residues from the lithium compounds were found in the recovered polymers. Although BuLi is expected to abstract the β-proton to give an olefin terminal, no such endgroups was detected at all in the product by ^1H NMR spectroscopy even under high sensitivity measurement. No further attempt was made to clarify whether or not the living end **5** was terminated by BuLi.

In contrast, the phenyl carbanions (LiC_6H_5 and $BrMgC_6H_5$) and the malonate anion [$NaCH(COOC_2H_5)_2$] instantaneously terminated the polymerization to give poly(IBVE) capped with a phenyl or a malonate group, respectively. ^1H NMR analysis showed the attachment of these end groups even at +60°C, as discussed later in this chapter; i. e., the number-average end functionality $\overline{F}_n$ was invariably very close to unity. Interestingly, these results indicate that delocalized and "soft" carbanions (phenyl and malonate) are better suited than localized and "hard" counterparts (primary carbanions) for end-capping the vinyl ether living end, which may also be a relatively "soft" carbocation in nature where the cationic charge is partially delocalized over the α-ether oxygen. In the following part of this study, therefore, sodiomalonic ester and phenyllithium were employed as end-capping agents.

2. Synthesis of X/COOH Telechelic Poly(IBVE) by Malonate End-Capping

2-1. End-Capping with Sodiomalonic Ester at High Temperature.

Besides the search of suitable end-capping agents for the base-stabilized living end **5**, another focus of this study was to synthesize telechelic poly(vinyl ethers) at high temperature above ambient where β-proton abstraction from living ends by end-capping agents would be more likely to occur. Thus, the end-capping with sodiomalonic ester was examined in detail in the IBVE polymerization with the

2d/$EtAlCl_2$ system at +60°C as well as at 0°C.[13] The recovered polymers gave ^1H NMR spectra identical with those reported for malonate capped poly(IBVE).[8,9]

The end-functionality $\overline{F}_n$ was determined from the NMR peak intensity ratio of the malonate methylene (4H, 4.2 ppm) to the poly(IBVE)'s pendant methyl (6H, 0.9 ppm). No evidence was available for the occurrence of the β-proton abstraction by the sodium salt, even at a temperature as high as +60°C.

In addition to the end-functionality $\overline{F}_n$, the number-avarage degree of polymerization [$\overline{DP}_n$(obd)] was determined from the ratio of the pendant methyl to the α-end methyl. Figure 1 plots the $\overline{F}_n$ and $\overline{DP}_n$(obd) of the polymers produced at different initiator concentrations at 0 and +60°C (conversion, ca. 100%).

For both temperatures, $\overline{DP}_n$(obd) was in good agreement with the calculated value (= $[IBVE]_0/[\mathbf{2d}]_0$) for living polymers in the range from 20 to 100. In this range, the MWDs of the products were very narrow ($\bar{M}_w/\bar{M}_n < 1.1$), though slightly broader at +60°C. For all these polymers, the end-functionality $\overline{F}_n$ was invariably close to unity. Even at +60°C, therefore, the **2d**/$EtAlCl_2$ initiating system generates living polymers that can be cleanly and quantitatively quenched by sodiomalonic ester to form malonate-capped polymers **3d**.

2-2. Synthesis of HO/COOH Hetero-Telechelic Poly(IBVE) (4a)

After establishing the feasibility of end-capping of the base-stabilized living end **5** with the malonate anion, the author synthesized a series of hetero- and homo-telechelic polymers **3** and **4** by this method at 0°C and even at +60°C (Scheme I), particularly focusing on its feasibility at high temperature (+60°C). As an initial example, hydroxy- and carboxy-capped hetero-telechelic poly(IBVE) **4a** was prepared. Thus, living IBVE polymerization was initiated with the acetate-functionalized initiating system **2a**/$EtAlCl_2$ [X: $OOCCH_3$] at 0 and +60°C in *n*-hexane solvent containing an excess of 1,4-dioxane (1.2 M), and the resultant living end **5a** was end-capped in situ with excess sodiomalonic ester. Figure 2 shows the MWDs of the polymers thus prepared as a function of the monomer-to-initiator ratio $[IBVE]_0/[\mathbf{2a}]_0$.

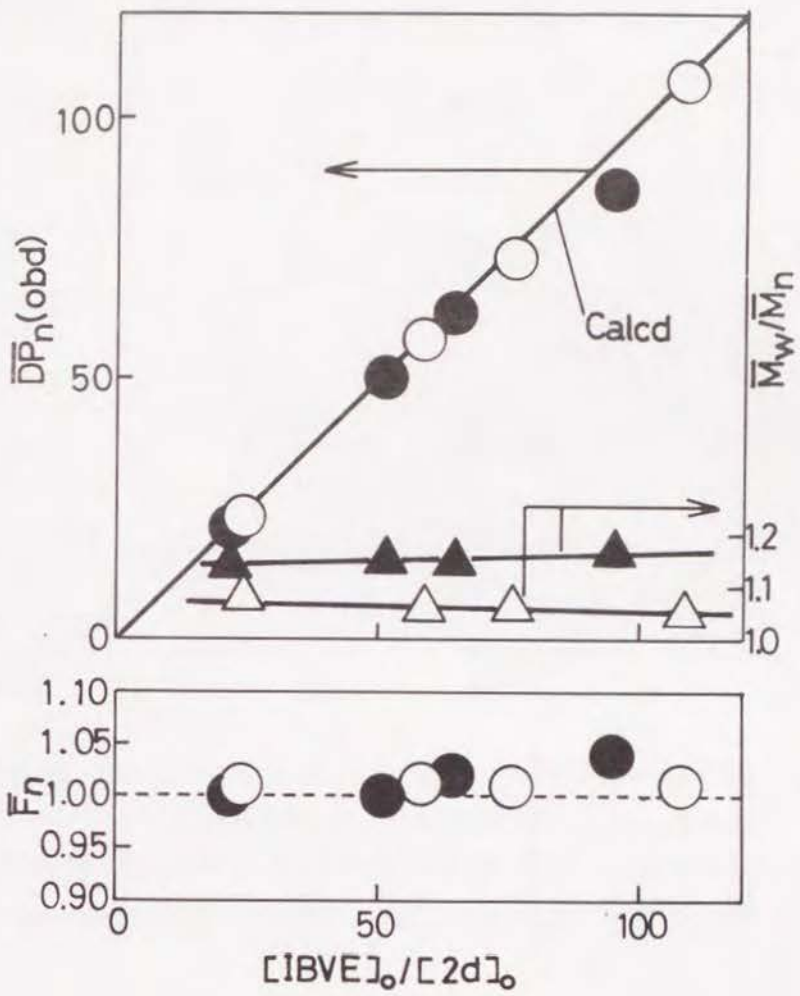


Figure 1. Effect of the initial **2d** concentration ($[\mathbf{2d}]_0$) on the $\overline{DP}_n$(obd), $\bar{M}_w/\bar{M}_n$, and $\overline{F}_n$ of malonate-capped polymers (**3d**) in the IBVE polymerization by **2d**/$EtAlCl_2$ in *n*-hexane at 0°C (○,△) and +60°C (●,▲): $[IBVE]_0$ = 0.76 M; $[\mathbf{2d}]_0$ = 7 – 35 mM; $[EtAlCl_2]_0/[\mathbf{2d}]_0$ = 1.0 (0°C) or 0.80 (+60°C); [1,4-dioxane] = 1.2 M; conversion~100 %.

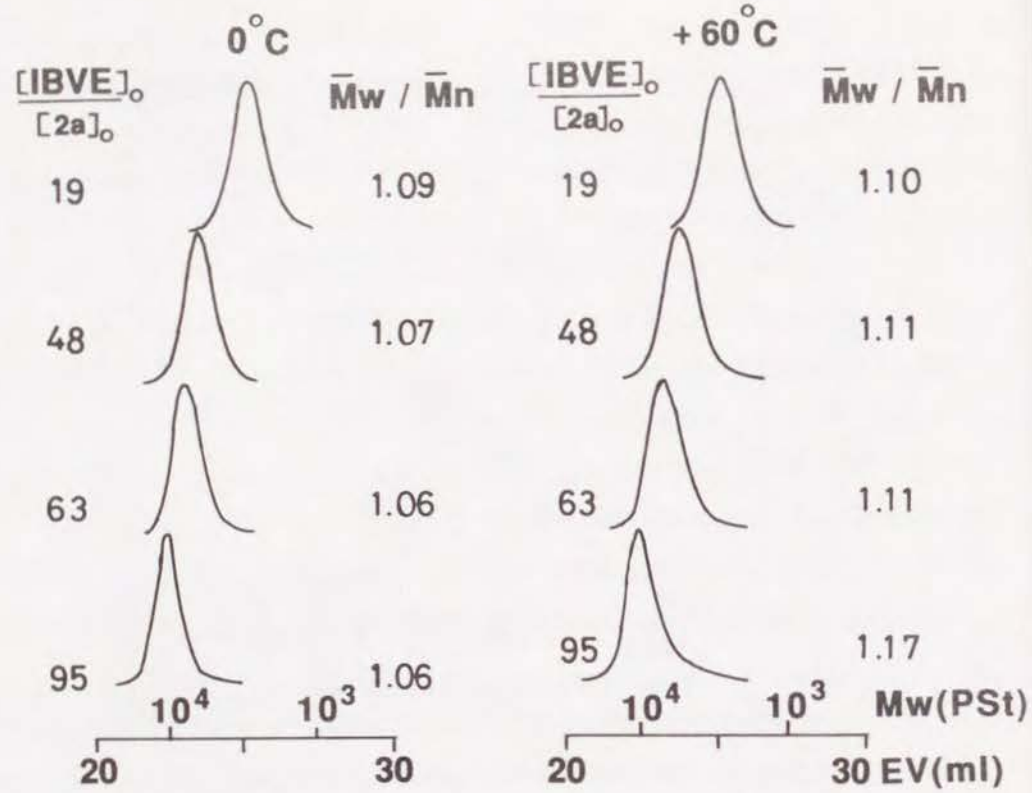


Figure 2. MWD of acetoxy/malonate hetero-telechelic polymers (**3a**); polymerization by **2a**/$EtAlCl_2$ in *n*-hexane at 0°C (A) and +60°C (B): $[IBVE]_0$ = 0.76 M; $[\mathbf{2a}]_0$ = 8-40 mM; [1,4-dioxane] = 1.2 M; $[EtAlCl_2]_0/[\mathbf{2a}]_0$ = 1.0 (0°C) or 0.80 (+60°C); conversion~100 %.

Irrespective of polymerization temperature and the $[IBVE]_0/[\mathbf{2a}]_0$ ratio, all the polymers possessed very narrow MWDs, and the molecular weight increased in direct proportion to the monomer-to-initiator feed ratio. Thus, living polymerization proved operatable even at +60°C with initiator **2a**, which carries a polar ester group.

A typical ^{1}H NMR spectrum of the end-capped polymer obtained at +60°C is given in Figure 3A. Consistent with the expected telechelic structure **3a**, all key

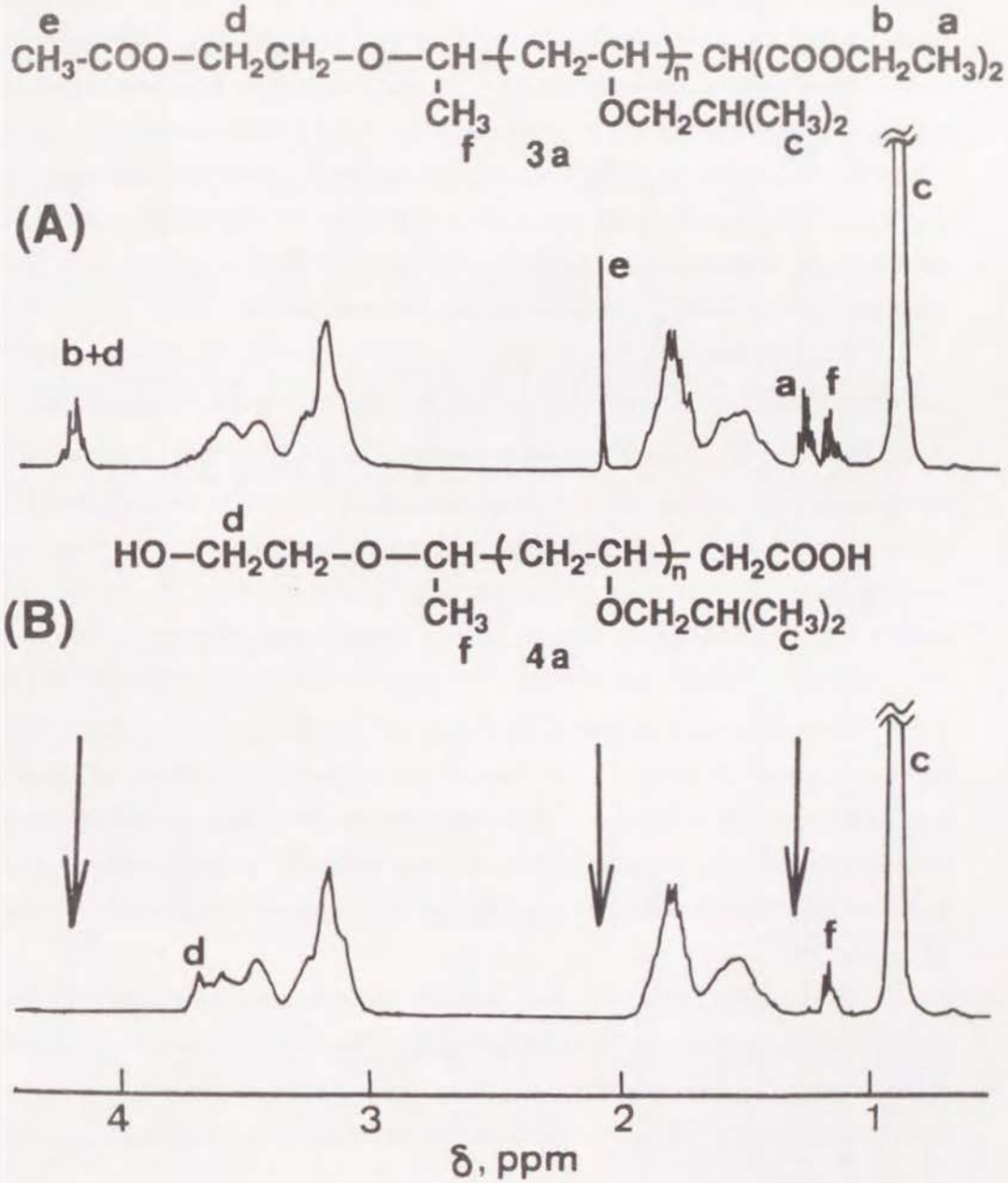


Figure 3. ^{1}H NMR spectra of hetero-telechelic polymers: (A) polymer **3a** obtained at +60°C (acetoxy/malonate; entry 5, Table II); (B) polymer **4a** (hydroxy/carboxy; from sample A).

absorptions of the poly(IBVE) main-chain (e.g., peak c), the α-end acetate (peaks d and e), and the ω-end malonate (peaks a and b) were seen, and absorptions indicative of by-products were absent. The $\overline{DP}_n$(obd) of **3a** was determined from the peak intensity ratio of the main-chain (peak c) to the terminal malonate (peak e) (Table II). The observed $\overline{DP}_n$ was in good agreement with the calculated value ($[IBVE]_0/[\mathbf{2a}]_0$) based on the assumption that one molecule of **2a** produces one polymer. The determination of $\overline{DP}_n$ by 270 MHz ^{1}H NMR is applicable to **3a** and other polymers with $\overline{DP}_n$ up to 100 (estimated error, ±10 %).

Based on the fact that [living end]$_0$ = [initiator **2**]$_0$, the end-functionality was determined from the ratio [end group]/[**2a**]$_0$ for both α-end acetate ($\overline{F}_n(\alpha)$) and ω-end malonate ($\overline{F}_n(\omega)$). The acetate content [CH_3COO-] (mol/L) was obtained from the NMR intensity ratio of the acetate methyl (peak e) to the poly(IBVE) pendant methyl (peak c). Similarly, the terminal malonate content was given by the ratio of peak b to c; because of the overlapping of peaks b and d, the integral of peak b was determined by subtracting the contribution of peak d, which was obtained from the integral of another α-end signal e [from the observed integral (b + d)]. Table II (entry 1-8) shows the $\overline{F}_n(\alpha)$ and $\overline{F}_n(\omega)$ values thus obtained for a series of polymer **3a** samples. Despite that these functionality values are based on the NMR signal ratios that are independant of each other, they are invariably very close to unity and thereby demonstrate the attachment of both one acetate and one malonate functions per polymer even for the samples produced at +60°C and with $\overline{DP}_n$ up to 100.

As shown in Figure 3B, both acetoxy and malonate terminals of **3a** could readily be transformed into the corresponding hydroxy and carboxy terminals (**4a**), respectively, by the standard alkaline hydrolysis, followed by thermal decarboxylation [Eq (1)].[6] The signals associated with the acetate (peaks d and e)

$$\mathbf{CH_3COO}\text{-}\!\sim\!\sim\!\mathbf{CH(COOC_2H_5)_2} \xrightarrow[\text{2) } H^{\oplus}/\Delta]{\text{1) } OH^{\ominus}} \mathbf{HO}\text{-}\!\sim\!\sim\!\mathbf{COOH} \qquad (1)$$

3a **4a**

Table II

Synthesis of Telechelic Poly(IBVE) (**3**) via End-Capping with $NaCH(COOC_2H_5)_2$ or LiC_6H_5[a]

Entry	Initiator	Functional Group		Temp	Time	$\overline{DP}_n$	$\overline{DP}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{F}_n(\alpha)$[b]	$\overline{F}_n(\omega)$[b]
		α-end	ω-end	(°C)	(min)	(calcd)	(obd)			
1	**2a**	$OCOCH_3$	$CH(COOC_2H_5)_2$	0	15	19	17	1.09	1.10	1.09
2				0	90	48	43	1.07	1.08	1.10
3				0	300	63	59	1.06	1.09	1.07
4				0	21hr	95	88	1.06	1.05	1.08
5				+60	1	19	19	1.10	1.02	1.03
6				+60	3	48	47	1.11	1.04	1.01
7				+60	6	63	60	1.11	1.06	1.06
8				+60	10	95	91	1.17	1.03	1.04
9[c]	**2b**	$N[COOC(CH_3)_3]_2$	$CH(COOC_2H_5)_2$	0	10	10	10	1.18	0.95	0.96
10[c]				+60	0.5	10	16	1.30	0.60	0.61
11	**2c**	$CH(COOC_2H_5)_2$	$CH(COOC_2H_5)_2$	0	15	19	18	1.08		2.18
12				+60	1	19	19	1.16		2.04
13[d]	**2c**	$CH(COOC_2H_5)_2$	C_6H_5	0	15	19	18	1.08	1.03	1.02
14[d]				+60	1	19	19	1.10	1.02	1.01

a) $[IBVE]_0$ = 0.76 M (10 vol%); $[\mathbf{2}]_0$ = 7.0 - 76.0 mM; $[EtAlCl_2]_0/[\mathbf{2}]_0$ = 1.0 (0°C) or 0.80 (+60°C) except for entry 9 and 10; [1,4-dioxane] = 1.2 M (10 vol%); conversion ~ 100%. Living polymers were quenched with sodiomalonic ester except for entry 13 and 14; [capping agent]/$[\mathbf{2}]_0$ = 10; End-capping reaction for 60 min.

b) Determined by ^{1}H NMR with an estimated error + 10 %; see text for details.

c) $[EtAlCl_2]_0/[\mathbf{2}]_0$ = 2.0

d) Quenched with LiC_6H_5.

and the malonate (peaks a and b) terminals are absent for the hydrolysis product. Polymer **4a** is the first example of hetero-telechelic poly(vinyl ether) with hydroxy and carboxy terminals, which may undergo condensation reactions with each other.

2-3. Synthesis of NH_2/COOH Hetero-Telechelic Poly(IBVE) (4b)

In a manner similar to the synthesis of **4a**, amino- and carboxy-capped hetero-telechelic poly(IBVE) **4b** was prepared [Scheme I and Eq (2)]. For this was employed a new initiator **2b** that carries a di-*t*-butoxycarbonylimido function,[2] which turned out better suited as an amine-protecting group than the phthalimide counterpart previously employed,[14] and IBVE was polymerized with the **2b**/$EtAlCl_2$ system in *n*-hexane containing 1,4-dioxane at 0 and +60°C. The resulting living end (**5b**)[14] was then end-capped with sodiomalonic ester to give hetero-telechelic precursor polymer **3b**.

Structural analysis of the products by ^1H NMR spectroscopy confirmed the structure expected for **3b** (Figure 4A). For example, the spectrum clearly showed signals assigned to the imido's methyl (α-end; the sharp singlet d) and the malonate's ethyl groups (ω–end; peaks a and b). The end-functionality $\overline{F}_n(\alpha)$ (terminal imide/polymer) was determined from the intensity ratio of peak d to b and the initial concentration of initiator **2b** (= [living end]); because of the overlapping of peak d and the adjacent peaks, the integral of peak d was determined by subtracting the contribution of these nearby peaks. $\overline{F}_n(\omega)$ (terminal malonate/polymer) was determined as already discussed for **3a** (see above), and their values are listed in Table II. For the sample obtained at 0°C (entry 9), both $\overline{F}_n(\alpha)$ and $\overline{F}_n(\omega)$ were close to unity, indicating the attachment of one imide and one malonate groups per polymer. For the synthesis at +60°C (entry 10), on the other hand, clearly lower $\overline{F}_n(\alpha)$ and $\overline{F}_n(\omega)$ values (~0.6) were obtained, and $\overline{DP}_n$(obd) value was higher than the calculated value.

The terminal imido and malonate groups of **3b** could readily be converted into an amino and a carboxy functions, respectively, to give hetero-telechelic polymer **4b** [Eq (2)]. The endgroups transformation consisted of alkaline hydrolysis/thermal decarboxylation on the malonate and subsequent acidolysis of the butoxycarbonylimide (with 6 N HCl).[2] Figure 4B illustrates a typical ^1H NMR

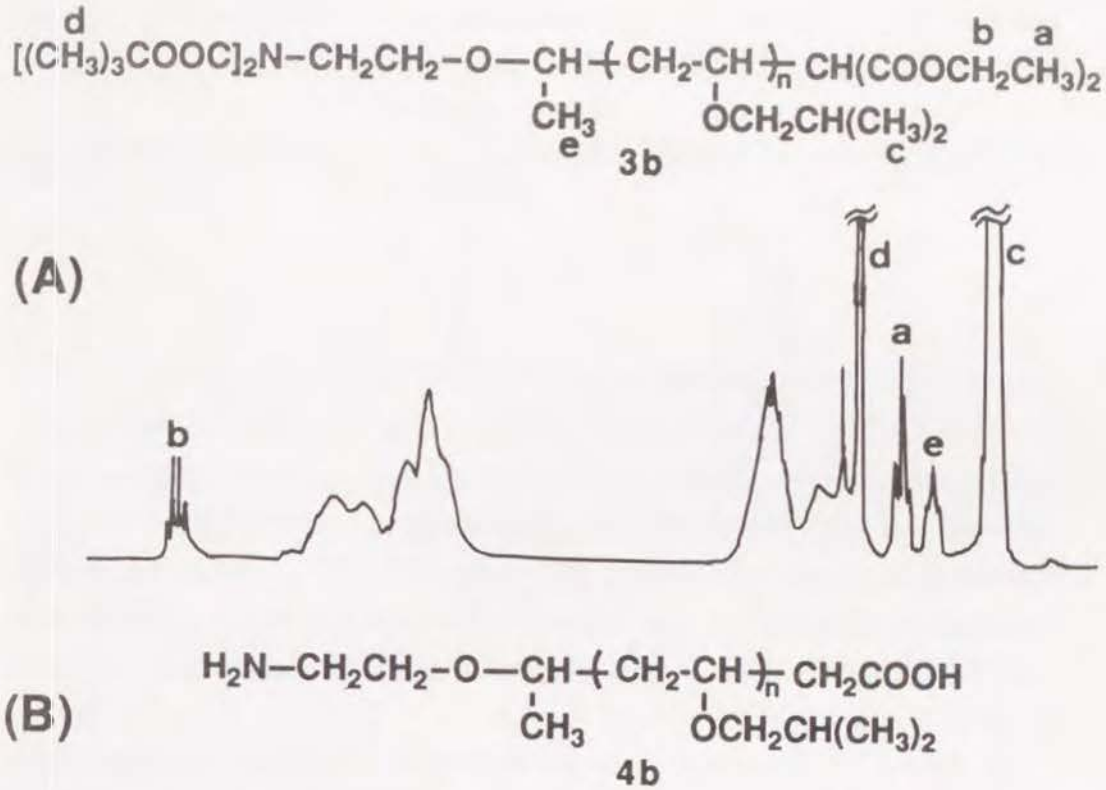
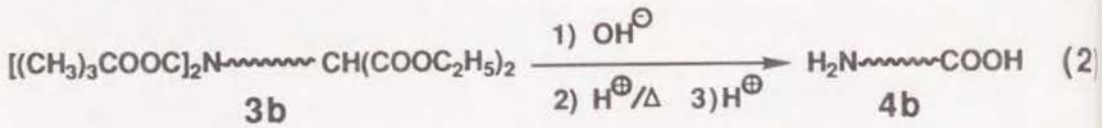


Figure 4. ^1H NMR spectra of hetero-telechelic polymers: (A) polymer **3b** obtained at 0°C (imido/malonate; entry 9, Table II); (B) polymer **4b** (amino/carboxy; from sample A).

spectrum of the product, which shows the complete absence of the precursor terminals (peaks a, b, and d in Figure 4A).



(2)

2-4. Synthesis of COOH/COOH Telechelic Poly(IBVE) (4c)

In addition to the OH/COOH (**4a**) and the NH_2/COOH (**4b**) hetero-telechelic polymers, the COOH/COOH homo-telechelic counterpart (**4c**) can also be prepared similarly (Scheme I). Although the same polymer has already been prepared at temperatures below 0°C on the bases of the HI/I_2 initiating system,[7] the use of the malonate-carrying initiator **2c** with $EtAlCl_2$ and 1,4-dioxane now permitted the synthesis to be operable well above room temperature, where the base-stabilized living species **5c** can survive.

The ^1H NMR spectrum of the malonate-quenched polymer obtained even at +60°C (Figure 5A) was fully consistent with the structure **3c**, as evidenced by absorptions a and b due to the α-end and ω-end malonates along with the α–end methyl signal d. $\overline{F}_n(\omega)$ was determined by comparing the concentration of the malonate groups (the intensity ratio of peak b to c) with the initial concentration of initiator **2c**. As shown in Table II (entry 11 and 12), the polymers, either obtained at 0 or +60°C, exhibited very narrow MWDs ($\overline{M}_w/\overline{M}_n < 1.1$) and $\overline{F}_n(\omega)$ values close to two. Accordingly, $\overline{DP}_n$(obd) values were in good agreement with the calculated values, indicating the formation of telechelic malonate-capped poly(IBVE) **3c** that has exactly two malonate groups per chain.

As already shown,[6] the conversion of the terminal malonates into two carboxy groups by hydrolysis/decarboxylation [Eq (3)] proceeded smoothly (Figure 5B). No difference was found between the samples of the biscarboxylate polymer **4c** obtained with the **2c**/$EtAlCl_2$/dioxane and the HI/I_2 systems.

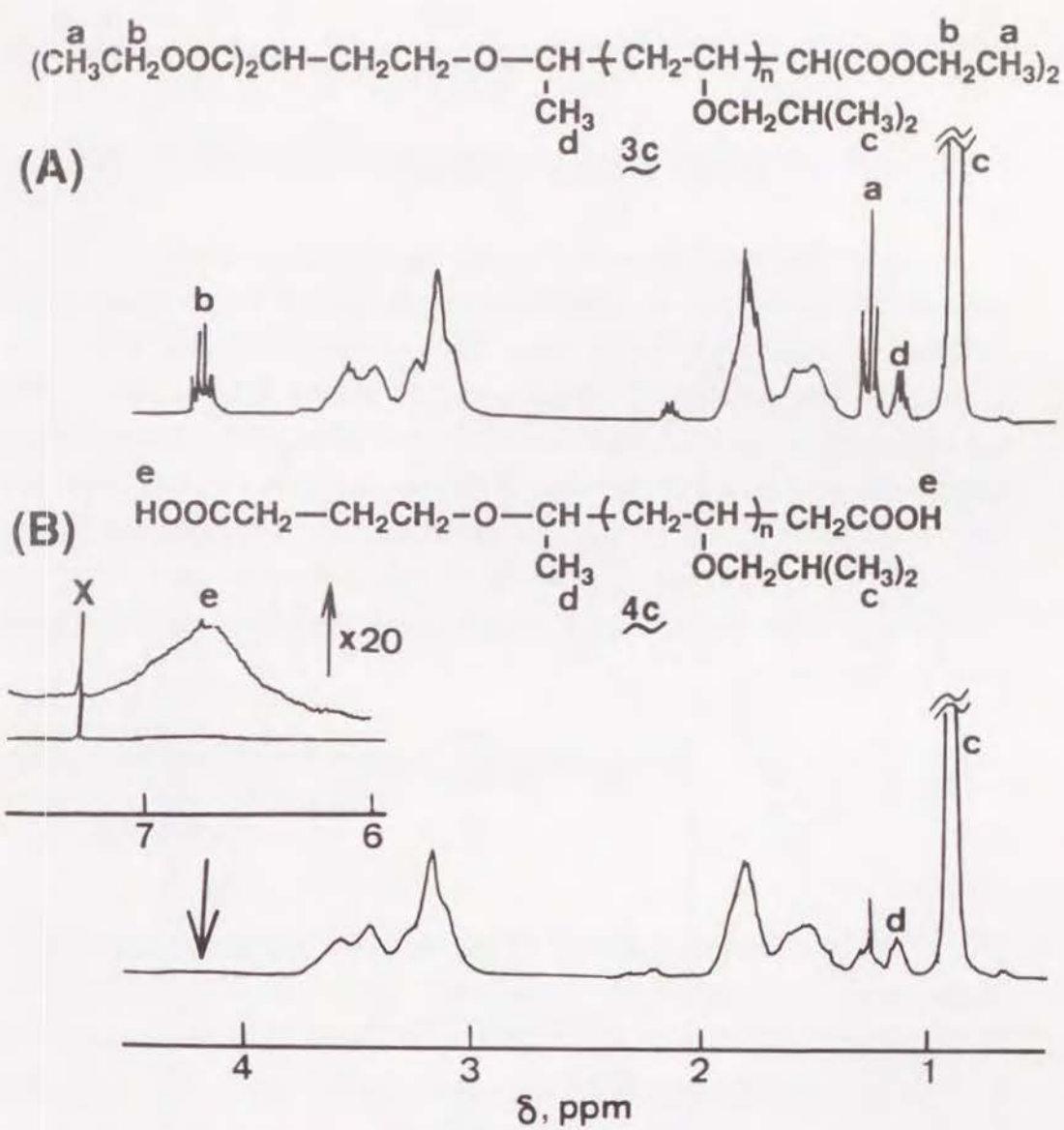


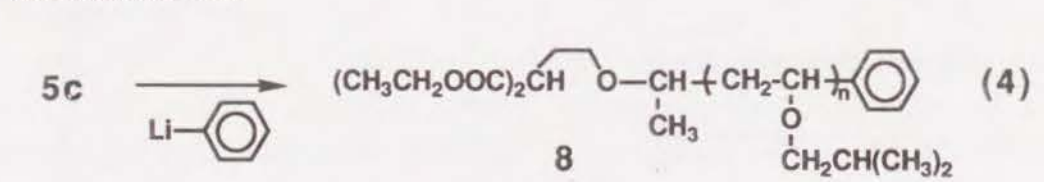
Figure 5. ^1H NMR spectra of homo-telechelic polymers:
(A) polymer **3c** obtained at +60°C (malonate; entry 12, Table II);
(B) polymer **4c** (carboxy; from sample A). The cross (X) indicates the signal due to a trace of $CHCl_3$ in $CDCl_3$ solvent.

$$(C_2H_5OOC)_2CH\text{-}\sim\sim\text{-}CH(COOC_2H_5)_2 \xrightarrow[2)\ H^{\oplus}/\Delta]{1)\ OH^{\ominus}} HOOC\text{-}\sim\sim\text{-}COOH \quad (3)$$

3c 4c

3. Synthesis of Hetero-telechelic Poly(IBVE) with Phenyl Terminal (8)

On the basis of the search for end-capping agents shown in Table I, terminal functionalization was also examined with use of the phenyl carbanion (LiC_6H_5) in place of the malonate anion. Thus, as typical examples, IBVE living polymers **5c** were generated by the malonate-type initiator **2c** along with $EtAlCl_2$ and 1,4-dioxane in *n*-hexane at 0°C and +60°C, and subsequently end-capped with phenyl lithium to give a phenyl-capped polymer **8** [Eq (4)]. This phenyl end-capping method is equally applicable to the living poly(IBVE) initiated with the other **2**/$EtAlCl_2$ systems. According to the conversion analysis by gas chromatography, the polymerization was terminated immediately after the addition of the lithium salt.



Structural analysis by ^1H NMR spectroscopy (Figure 6) confirmed the formation of malonate/phenyl hetero-telechelic polymer **8**, as evidenced by the signals of the α-end malonate group (peak a and b) and the ω-end phenyl group (peak e), along with the poly(IBVE) main-chain signals (peak c, etc.). $\overline{F}_n(\alpha)$ was determined from the concentration of the malonate group (the intensity ratio b/c), and $\overline{F}_n(\omega)$ from the concentration of the phenyl group (intensity ratio e/c), both compared with $[\mathbf{2d}]_0$. $\overline{DP}_n$(obd) was determined from the peak intensity ratio of the main-chain protons (peak c) to the malonate protons (peak b). Table II shows that the polymers, obtained at either 0 or +60°C, possess a very narrow MWD, $\overline{F}_n(\alpha)$ and $\overline{F}_n(\omega)$ close to unity, and $\overline{DP}_n$(obd) value being in good agreement with the calculated value ($[IBVE]_0/[\mathbf{2d}]_0$). All these data corroborate the quantitative attachment of one malonate and one phenyl groups per polymer. The malonate

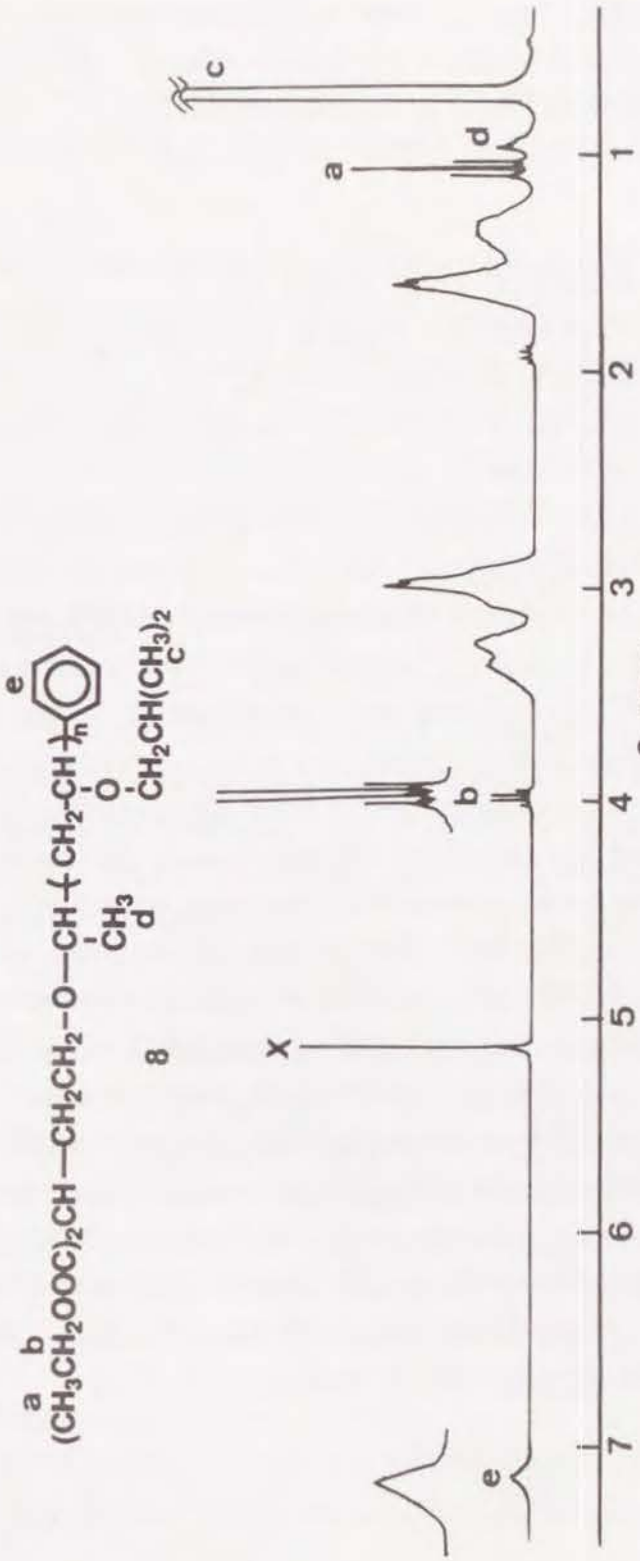


Figure 6. ^1H NMR spectrum of malonate/phenyl hetero-telechelic poly(IBVE) **8** obtained at +60°C (entry 14, Table II). The cross (X) indicates the peak due to a trace of CH_2Cl_2 in CD_2Cl_2 solvent.

terminal can be converted into the acid form without deteriorating the phenyl end group. The terminal phenyl moiety would prove useful as a versatile site for attaching functional groups via Friedel-Crafts and other reactions.

EXPERIMENTAL

Preparation of Functionalized Vinyl Ethers (1)

2-Acetoxyethyl vinyl ether (**1a**)[15] and diethyl 2-vinyloxyethyl malonate (**1c**)[6] were prepared according to the literature methods.

Di-*t*-butyl *N*-[2-(vinyloxy)ethyl]imidedicarboxylate (**1b**) was prepared as follows. In a 300 mL, three-necked, round-bottom flask fitted with a magnetic stirrer, a reflux condenser, and a dropping funnel were charged di-*t*-butyl iminodicarboxylate, $HN[CO_2C(CH_3)_3]_2$ (10.0 g, 46 mmol) (Aldrich, purity 95%), sodium hydroxide aqueous solution (1 M, 43 mL, 43 mmoL NaOH), and dimethyl sulfoxide (100 mL). After stirred for 1 h at room temperature, the reaction mixture was then warmed to 80°C in an oil bath, and 2-chloroethyl vinyl ether (9.2 g, 92 mmoL) and tetra-*n*-butylammonium bromide (1 g; a phase-transfer catalyst) were added. The heterogeneous solution was stirred at this temperature for 6 h, cooled to room temperature, and then poured into 500 mL of water. The aqueous phase was extracted with three 50-mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed twice with water (100 mL each) and evaporated under reduced pressure to give a yellowish viscous liquid. The crude product was purified by preparative size-exclusion chromatography (column: Shodex 2001 polystyrene gel; solvent: $CHCl_3$); the collected fractions in chloroform was dried with sodium sulfate overnight and evaporated to dryness under reduced pressure to give **1b** as a light yellowish viscous liquid: yield, 60 %; purity > 98 % by ^1H NMR; ^1H NMR ($CDCl_3$): δ 6.44 (q, 1H, =CH-), 4.11 (m, 2H, CH_2=), 3.86 (t, 4H, -CH_2CH_2-), 1.50 (s, 18H, C-CH_3); ^{13}C NMR ($CDCl_3$): δ 152.4 (C=O), 151.4 (=CH), 86.7 (CH_2=), 82.2 (-C-), 66.0 (O-CH_2), 44.9 (CH_2-N), 27.9 (C-CH_3).

Initiators (2)

Functionalized initiators (**2a-2d**) were prepared from trifluoroacetic acid and the corresponding vinyl ethers (**1**), as described already.[2]

Capping Agents

Diethyl sodiomalonate (200 mM in 1,4-dioxane) was prepared as reported.[6] Acetaldehyde 3-lithiopropyl ethyl acetal (**6**) and 2-lithioethoxytrimethylsilane (**7**) were synthesized by lithiating the corresponding bromides according to the method of Dias and McCarthy.[8] *n*-Butyllithium (1.6 M in tetrahydrofuran) and phenyllithium [1.8 M in a cyclohexane-ether (70/30, v/v) mixture] were of commercial source (Aldrich) and were used under dry nitrogen without further purification.

Other Materials

IBVE (monomer), ethyl vinyl ether (**1d**), *n*-hexane (polymerization solvent), 1,4-dioxane (added base), and *n*-heptane (internal standard for gas chromatography) were purified by the usual methods[5,11] and distilled twice over calcium hydride just before use. Commercial $EtAlCl_2$ (Kanto Chemicals; 1.0 M in *n*-hexane) and CF_3COOH (Wako Chemicals; > 99 %) were used under dry nitrogen without further purification.

Procedures

Polymerization was performed under dry nitrogen in baked glass tubes each equipped with a three-way stopcock. The reactions were initiated by sequencial addition of the initiator **2** and $EtAlCl_2$ solutions (0.50 mL each) into a monomer solution (4.0 mL in *n*-hexane) containing 1,4-dioxane (0.50 mL, 1.2 M, 10 vol%) at 0 or +60°C. The resulting living polymers were terminated with solutions of a capping agent (see Table I), which was 10-fold molar excess over the initiator (**2**). The recovery and purification of the polymers were done as described already.[2]

Deprotection

Regardless of the α-end function X, the malonate-capped poly(IBVE) (**3a** - **3c**) (100 mg) was dissolved in ethanol (10 mL), and hydrolysis/decarboxylation

was carried out as reported.[6] For X = $OCOCH_3$ (**3a**) and $CH(COOC_2H_5)_2$ (**3c**), the hydrolysis/decarboxylation led to the fully deprotected telechelic polymers, **4a** (OH/COOH) and **4c** (COOH/COOH). For X = $N[COOC(CH_3)_3]_2$ (**3b**), the decarboxylation product was dissolved in nitromethane (20 mL) and treated with 6 N hydrochloric acid (50-fold molar excess over the imide function in the polymer) for 6 h at room temperature with stirring. The reaction mixture was washed sequentially with NaOH aqueous solution (equiv to the hydrochloric acid employed) and water, isolated by evapolation, and finally dried in vacuo to give **4b** (NH_2/COOH terminals).

Polymer Characterization

The MWD of the polymers was measured by size-exclusion chromatography in chloroform at room temperature on Jasco Trirotar chromatograph equipped with three polystyrene gel columns (Shodex; exclusion limits: K-802, 5×10^3; K-803, 7×10^4; K-804, 4×10^5) that were calibrated against 12 standard polystyrene samples. The $\bar{M}_w/\bar{M}_n$ of the polymers were calculated from size-exclusion eluograms. ^{1}H NMR spectra were recorded at 270 MHz in $CDCl_3$ at room temperature on a Jeol GSX-270 spectrometer. DP_n was determined by ^{1}H NMR end-group analysis (see Results and Discussion).

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CHAPTER 3

TELECHELIC POLYMERS OF *p*-METHOXYSTYRENE WITH HI/ZnI_2

ABSTRACT

A series of end-functionalized polymers (**4**, **8**, and **9**) of *p*-methoxystyrene (pMOS) were synthesized by two methods based on living cationic polymerizations with hydrogen iodide-based initiating systems in toluene at -15°C: (1) (functional initiator method) living polymerization initiated with a functional vinyl ether-hydrogen iodide adduct [X-$CH_2CH_2OCH(CH_3)$-I] in conjunction with ZnI_2 to give α-end functional polymer **4**; and (2) (end-capping method) quenching the HI/ZnI_2-initiated living poly(pMOS), with a functional alcohol (HO-CH_2CH_2Z) to give ω-end functional polymer **8**.

X-$CH_2CH_2OCH(CH_3)$ -$(pMOS)_n$-OCH_3 (**4**)

[X: CH_3COO-(**4a**); $(EtOCO)_2CH$-(**4b**); phthalimide (**4c**)];

H -$(pMOS)_n$-OCH_2CH_2-Z (**8**)

[Z: -$OCOCH_3$(**8a**); -$OCOC(CH_3)=CH_2$(**8b**); -$OCOCH=CH_2$(**8c**)]

Combination of the two methods gave hetero-telechelic poly(pMOS); e.g., **9** with a malonate and a methacrylate terminals:

$$(EtOCO)_2CHCH_2CH_2O\overset{CH_3}{\overset{|}{C}}H\text{-}(pMOS)_n\text{-}OCH_2CH_2OCO\overset{CH_3}{\overset{|}{C}}=CH_2 \quad (\mathbf{9})$$

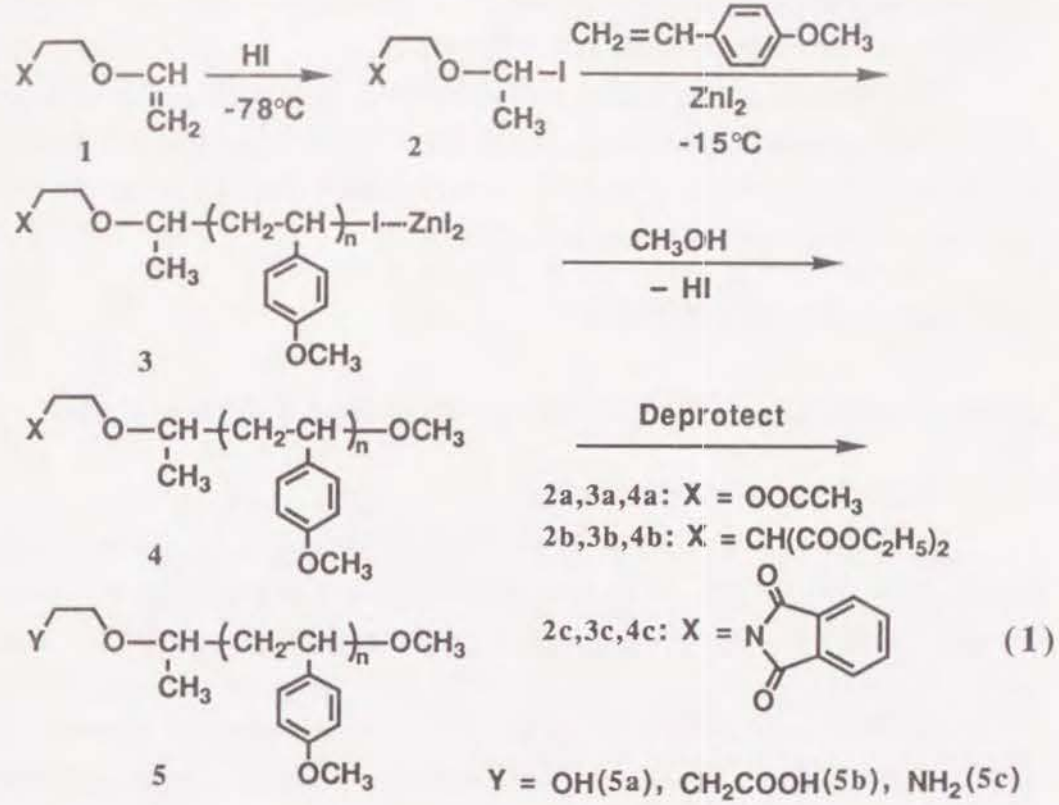
^1H NMR analysis showed all these polymers to possess controlled molecular weights ($\overline{DP}_n=[pMOS]_0/[initiator]_0$) and end-functionalities close to 1 or 2. The end groups of polymers **4a**-**4c** and **8a** can be converted into hydroxyl (**4a** and **8a**), carboxy (**4b**), and amino (**4c**) functions, whereas polymers **8b**, **8c** and **9** are new (meth)acrylate-type macromonomers with a rigid poly(pMOS) chain.

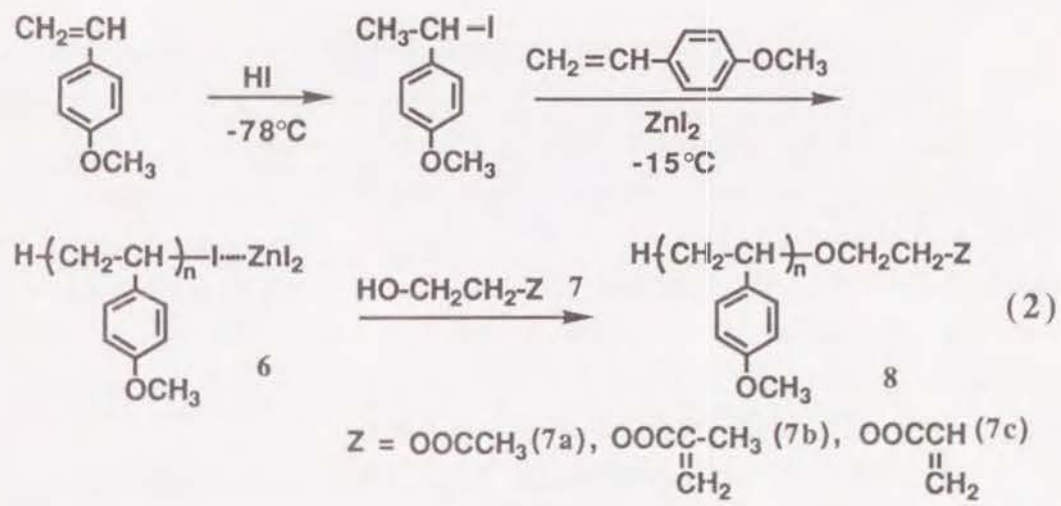
INTRODUCTION

Living polymerization has been among the most effective methods for the controlled synthesis of end-functionalized polymers and oligomers. In living cationic polymerization of vinyl monomers, the hitherto prepared end-functional polymers[1]are of flexible backbones primarily derived from vinyl ethers[2-10] and isobutylene;[11,12] some new examples of end-functionalized poly(vinyl ethers) have been given in Chapters 1 and 2.[4] Rather surprisingly, few have been known for their counterparts of rigid backbones, particulaly those from styrene derivatives, in marked contrast to the ample examples that have been obtained by living anionic polymerization.[13]

Recently, Higashimura et al. have achieved living cationic polymerizations of *p*-methoxystyrene (pMOS)[14] and *p*-*t*-butoxystyrene[15] with use of the hydrogen iodide/zinc iodide (HI/ZnI_2) initiating system. This and the following Chapters (3 and 4) are concerned with the synthesis of end-functionalized poly(*p*-alkoxystyrenes) based on these living cationic processes and two methods of end-functionalization originally developed for vinyl ethers:[2,3a] In one method [Eq (1)], living polymerization of a *p*-alkoxystyrene is initiated by an initiator carrying a functional group (X) to be incorporated into the polymer as a "head"(α-end) group (functional initiator method). Herein typical "functional initiators" are the adducts (**2**) of hydrogen iodide with vinyl ethers (**1**) carrying a pendant function X.[1-3] The other method [Eq (2)] utilizes the quenching of the HI/ZnI_2-initiated living poly(*p*-alkoxystyrene) with a reagent (**7**) having a functional group (Z) to be attached to the polymer "tail" (ω-end) (end-capping method).[3a]

Though these two methods are identical in principle with those for vinyl ethers (see Chapter 1 and 2),[4] their applicability to *p*-alkoxystyrenes is not straightforward and may depend on a few factors. As to the functional initiator method [Eq (1)], for example, it is unknown whether the vinyl ether-derived initiators **2**, coupled with ZnI_2, can indeed initiate (living) cationic polymerization of *p*-alkoxystyrenes, which are less reactive than alkyl vinyl ethers. As to the end-capping method [Eq (2)], it is unknown which types of nucleophiles are suited for clean and quantitative end-capping upon the growing *p*-alkoxystyryl carbocations,





which are less stable and hence more prone to β-proton elimination by the added quenchers than the corresponding vinyl ether cations.

The objectives of this chapter are to uncover these specific problems for *p*-methoxystyrene (pMOS) in the synthesis of a series of end-functionalized poly(pMOS) by the proposed two methods. A wide variety of α- and ω-end functions were examined, as shown in Eq (1) and (2).

RESULTS AND DISCUSSION

1. End-Functionalized Poly(pMOS) by Functional Initiator Method

1-1. Living Cationic Polymerization

As illustrated in Eq (1), a series of end-functionalized poly(pMOS) (**4a**-**4c**) were prepared with use of functional initiators (**2a**-**2c**), which were the adducts of hydrogen iodide with vinyl ethers (**1**) carrying functional pendant groups X. Thus, pMOS was polymerized in toluene at -15°C with the three initiators (**2**) in conjunction with ZnI_2 (a half equiv. to **2**). The functional group X in initiator **2** included acetoxy (**2a**), malonate (**2b**), and imide (**2c**), which are, respectively, the protected forms of hydroxy, carboxy, and amino groups. Despite the recent success in polymerizing pMOS from the HI/ZnI_2-generated living poly(vinyl ether),[16] the polymerization of pMOS with an initiator derived from a vinyl ether is not known yet.

Preliminary experiments soon revealed that the initiator **2**, prepared at -78°C, should be mixed with monomer and then with ZnI_2 at the same low temperature. If the adducts **2**, ZnI_2, and pMOS are mixed at -15°C (the polymerization temperature), living poly(pMOS) still forms but its end-functionality is below 1.0, apparently because at -15°C the HI-adduct partially releases hydrogen iodide that initiates a non-functionalized pMOS chains. Thus, all the experiments described herein were carried out by mixing **2**, monomer, and ZnI_2 at -78°C, keeping the reaction mixture for 20 hr at the same temperature, and then gradually warming it to -15°C where the polymerization occurred.

Figure 1 shows the time-conversion curves, the number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) for the polymers obtained with three

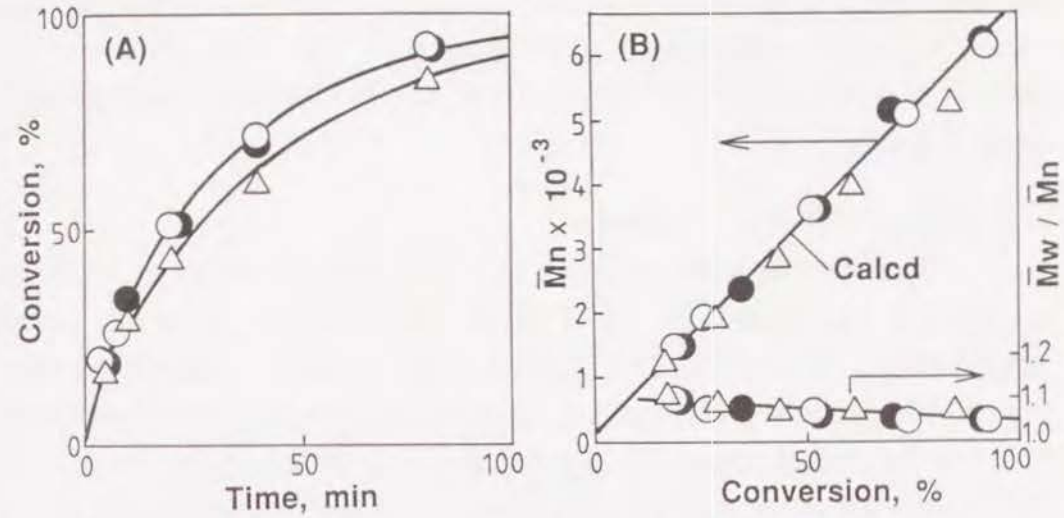


Figure 1. Time-conversion curves (A) and $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ (B) of pMOS obtained with the X-$CH_2CH_2OCH(CH_3)I$ (**2**)/ZnI_2 initiating systems in toluene at -15°C. X: (**O**) $OCOCH_3$; (●) $CH(COOC_2H_5)_2$; (Δ) phthalimide. $[pMOS]_0 = 0.50$ M; $[2]_0 = 10.0$ mM; $[ZnI_2]_0 = 5.0$mM. The intercept on the $\bar{M}_n$ axis indicates the molecular weight of pMOS monomer (= 134).

2/ZnI_2 initiating systems. The polymerizations proceeded quantitatively, where the overall reaction rates were almost independent of the functional groups X of the initiator **2** (Figure 1A). This fact is consistent with the polymerization pathway shown in Eq (1). Namely, regardless of the functional group X of the initiators, all the initiating systems lead to the identical growing active sites, once the initiation has been completed.

The $\bar{M}_n$'s of the polymers increased in direct proportion to monomer conversion and were virtually independent of the kind of initiators. The observed $\bar{M}_n$'s, though determined relative to standard polystyrenes, were in good agreement with the calculated values based on the assumption that one polymer chain forms

per unit initiator. In addition, the $\overline{M}_w/\overline{M}_n$ ratios remained unchanged and well below 1.1 at all conversions. These facts show the living nature of the polymerization of pMOS initiated by the **2**/ZnI_2 system, despite the polar functional group X therein.

1-2. Polymer Characterization

The end-group structure of the polymers was determined by ^1H NMR spectroscopy (see below). Figure 2A depicts the ^1H NMR spectrum of a typical sample of the acetoxy-capped poly(pMOS) obtained with the **2a**/ZnI_2 initiating system. The spectrum exhibits all key absorptions of the poly(pMOS) main-chain (a and b), the acetoxy group of the initiator fragment (d, e, and f), and the methoxy terminal (c)[20] that is derived from termination with methanol; absorptions indicative of by-products resulting from protonic impurities are completely absent. All these observations are consistent with the expected structure of **4a**.

The number-average degree of polymerization ($\overline{DP}_n$) for **4a** was determined from the peak intensity ratio of the pendant methoxy or the phenyl groups to the terminal methoxy (a/c or b/c). As shown in Table I, $\overline{DP}_n$'s were in good agreement with the calculated values ($\overline{DP}_n = [pMOS]_0(\%\ conv/100)/[\mathbf{2a}]_0$), which were based on the assumption that one living chain is formed from one molecule of **2a**. After the living nature of the polymerization (i.e. the absence of chain transfer and termination) had thus been established, the number-average end-functionality ($\overline{F}_n$) of the terminal (α-end) acetate for **4a** was determined by comparing its integrated ^1H NMR peak area with that of the ω-end methoxy group (ratios d/c and e/c). Though determined from the intensity ratios independent of each other, $\overline{F}_n$ was invaluably close to unity, indicating the formation of acetoxy-capped poly(pMOS) **4a** that has exactly one acetate group per chain.

Very similar results were obtained for the polymers (**4b** and **4c**) synthesized with the initiator that carries an ethyl malonate (**2b**) or a phthalimide (**2c**) pendant group. The ^1H NMR spectra of **4b** and **4c** are shown in Figures 2B and 2C, respectively. Table I shows the $\overline{DP}_n$(obd) and the $\overline{F}_n$ of these polymers.

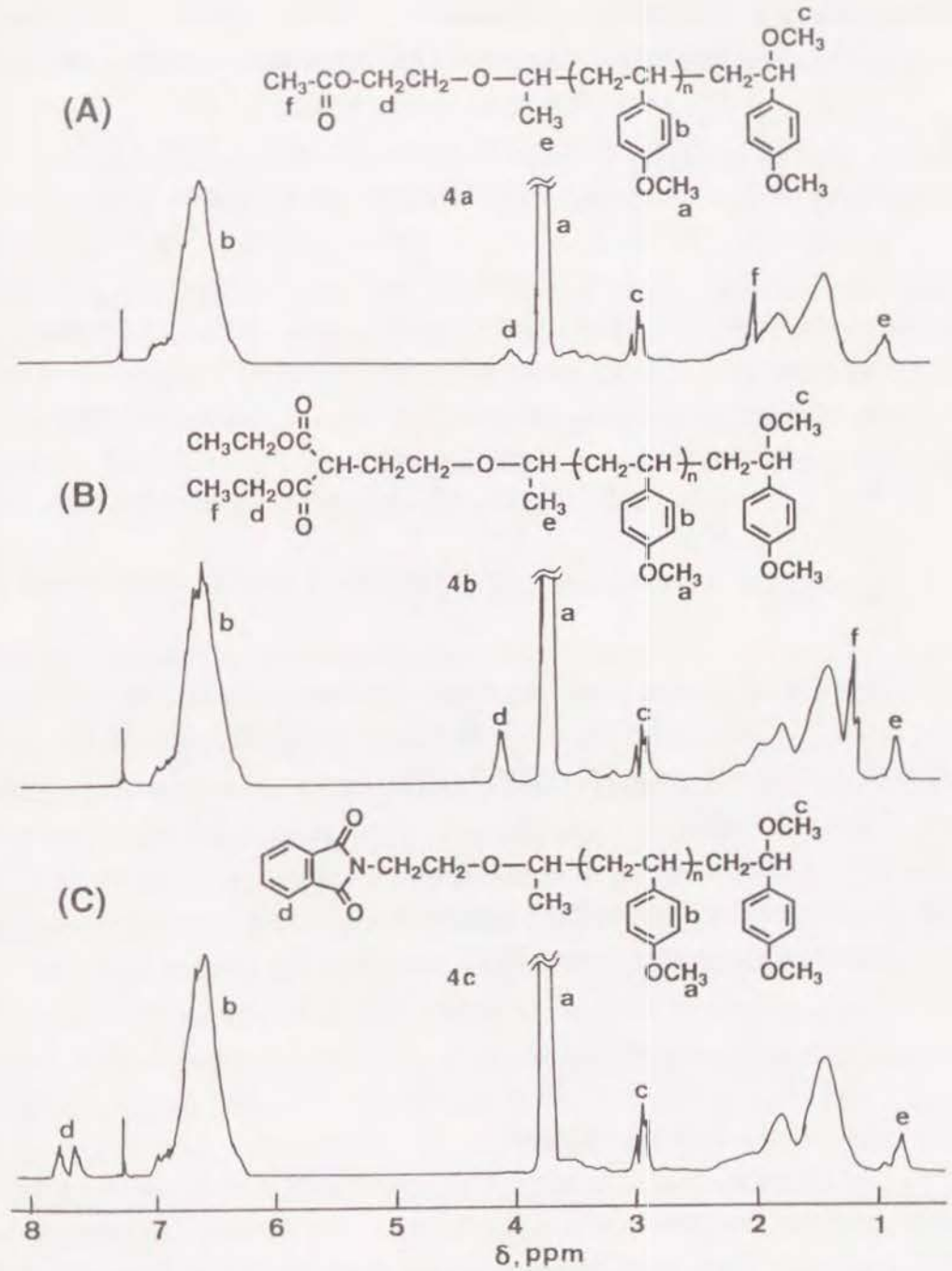
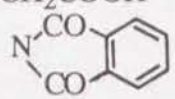


Figure 2. ^1H NMR spectra of end-functionalized poly(pMOS) (**4**): (A) acetoxy-capped, **4a**; (B) malonate-capped, **4b**; (C) imido-capped, **4c.**; see entry 1 – 3, Table I.

Table I

Synthesis of End-Functionalized Poly(pMOS) (**4** and **5**) by the Functional Initiator Method:[a]

Entry	Code	X	$\overline{DP}_n$(calcd)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\overline{DP}_n$(obd)[d,e]		$\bar{F}_n$[d,f]	
						a/c	b/c	d/c	e/c
1	**4a**	$OOCCH_3$	13.2	1960	1.08	13.5	13.6	0.99	1.01
	5a	OH		1830	1.10				
2	**4b**	$CH(COOEt)_2$	14.0	2120	1.09	14.1	14.3	0.99	0.99
	5b	CH_2COOH		1900	1.11				
3	**4c**		14.5	1850	1.12	14.5	14.6	0.96	0.99
	5c	NH_2		1720	1.15				

a) Polymerization were carried out in toluene at sequentially -78°C (24 h) and -15°C (10 min). $[pMOS]_0 = 0.50$ M; $[\mathbf{2}]_0 = 10$ mM; $[ZnI_2]_0 = 5$ mM.

b) $\overline{DP}_n(calcd) = (\%\ conv/100)\ [pMOS]_0/[\mathbf{2}]_0$.

c) Measured by SEC.

d) ^1H NMR peak intensity ratio; see Figure 2.

e) Number-average degree of polymerization.

f) Number-average end functionality.

1-3. End-Group Transformation

As shown in Eq (1), the terminal functional groups of the polymers **4a**-**4c** were converted into the corresponding hydroxy (**5a**), carboxy (**5b**), and amino (**5c**) terminals. Thus, for example, a sample of **4a** (shown in Figure 2A) was hydrolyzed under mild alkaline conditions (see Experimental). The signals d and f, associated with the acetate terminal (4.10 and 2.05 ppm, respectively; see Figure 2A), are absent in the hydrolysis product, indicating the formation of the hydroxy-

capped poly(pMOS) **5a**.[4] The sturucture, $\overline{DP}_n$, and MWD of the poly(pMOS) backbone remained unchanged during the end-group transformation, as seen in Table I.

In a similar manner, the α-end malonate of **4b** was converted into the corresponding carboxy group by the alkaline hydrolysis, followed by thermal decarboxylation.[3a] The signals associated with the malonate terminal (1.25 and 4.15 ppm; see Figure 2B) are absent in the hydrolysis/decarboxylation product, indicating the formation of the carboxy-capped poly(pMOS) **5b**. Furthermore, **4c** was hydrazinolyzed, where the peak d due to the imide terminal (7.70 ppm ; see Figure 2C) disappeared, to give the amino-capped poly(pMOS) **5c**.[5] The data shown in Table I (entry 1-3) corroborate that the poly(pMOS) backbones of these polymers were kept intact during the transformation processes.

2. End-Functionalized Poly(pMOS) by End-Capping Method.

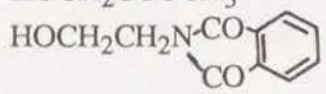
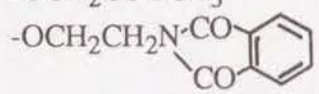
Search of End-Capping Agents

In the second part of this study, end-functionalized poly(pMOS) was synthesized by the end-capping method using "functional" capping agents [Eq (2)]. As reported previously, some delocalized carbanions (malonate[3,4] and phenyl[4]) and enolates[10] react quantitatively with living poly(vinyl ether) growing ends to give stable terminal groups, but it remains unknown, in general, which types of basic compounds are suited for living poly(pMOS) ends. The criteria for these quenchers include (a) quantitative attachment to a polymer end, (b) absence of side reactions such as β-proton elimination, and (c) formation of stable terminal groups. In this regard, a wider variety of capping agents may be applicable to poly(pMOS) than to poly(vinyl ethers). In particular, alcohols and amines are not best suited for the latter polymers because they lead to rather unstable acid-sensitive acetal and aminoether terminals, respectively, but such problems are not relevant to poly(pMOS).

With these points in mind, the author first examined sodiomalonic ester (carbanion salt) and a series of alcohols (prim, sec, and tert) as possible capping agents for a pMOS (Table II). Thus, living cationic polymerization of pMOS was

Table II

End-Capping Reactions of Living Poly(pMOS) with Various Capping Agents[a]

Entry	Capping Agent	End Group	$\bar{F}_n$[b]
4	$NaCH(COOC_2H_5)_2$	$-CH(COOC_2H_5)_2$	0
5	$HOC(CH_3)_3$	$-OC(CH_3)_3$	0
6	$HOCH(CH_3)_2$	$-OCH(CH_3)_2$	0.98
7	$HOCH_3$	$-OCH_3$	0.99
8	$HOCH_2CH_2OCOCH_3$	$-OCH_2CH_2OCOCH_3$	0.98
9	$HOCH_2COOCH_3$	$-OCH_2COOCH_3$	0
10			0.82

a) Polymerization with HI/ZnI_2 in toluene at -15°C; $[pMOS]_0$ = 0.38 M; $[HI]_0$ = 19 mM; $[ZnI_2]_0$ = 6 mM; conversion ~ 100 %; [capping agent]$_0$ > 190 mM.

b) $\bar{F}_n$ = [end group]/[α-CH_3] by ^1H NMR.

carried out with use of the HI/ZnI_2 initiating system in toluene at -15°C,[14] and near at 100% conversion, it was terminated by adding a solution of a capping agent in a large excess over the living ends (usually, [living end]/[capping agent] = 1/50). The number-average end-functionality ($\bar{F}_n$) of the ω-end was determined by comparing ^1H NMR peak intensity ratios of the methyl protons (Figure 2A, peak e; arising from the hydrogen iodide initiator) to the protons of the ω-end from the capping agent; note that the number of the living polymer (**6**) is equal to that of the hydrogen iodide initiator.

As shown in Table II, among the four basic compounds employed in our primary search (entry 4-7), sodiomalonic ester and *t*-butanol did not react with the

Table III

Synthesis of End-Functionalized Poly(pMOS) (**8**) by the End-Capping Method:[a]

Entry	Code	Z	$\overline{DP}_n$(calcd)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\overline{DP}_n$(obd)[d,e] a/c	b/c	$\bar{F}_n$[d,f] d/c	e/c	f/c
11	**8a**	$OOCCH_3$	23.8	2910	1.07	23.6	23.7	0.98		
12	**8b**	$OOCC(=CH_2)$	18.9	2560	1.07	19.0	19.1	1.00	0.98	
13	**8c**	$OOCCH(CH_3)=CH_2$	16.9	2330	1.07	16.7	16.6	1.03	0.98	0.99

a) Polymerizations were carried out in toluene at -15°C. $[pMOS]_0$ = 0.50 M; $[HI]_0$ = 21-30 mM; $[ZnI_2]_0$ = 5.0 mM; conversion ~ 100 %.

b) $\overline{DP}_n$(calcd) = $[pMOS]_0/[HI]_0$.

c) Measured by SEC.

d) ^1H NMR peak intensity ratio; see Figure 3.

e) Number-avarage degree of polymerization.

f) Number-avarage end functionality.

growing end, whereas the primary and the secondary alcohols (methanol and isopropanol, respectively) underwent quantitative reactions to give alkoxy terminals. The ineffectiveness of the malonate anion is in sharp contrast to its clean attachment to living poly(vinyl ether) ends[3,4]; the results for the three alcohols indicate that the bulky tertiary alcohol can not react with the relatively crowded poly(pMOS) cation carrying a phenyl and a polymer backbone.

On the basis of these results, the author then examined, as functional capping agents, three primary alcohols that carry protected forms of hydroxy, carboxy, and amino functions (entry 8-10). Though having essentially the same alcoholic moieties, however, only 2-hydroxyethyl acetate underwent a quantitative end-capping (entry 8); methyl hydroxyacetate was totally ineffective at all (entry 9);

and 2-hydroxyethyl phthalimide resulted in a partial attachment only. In all these cases, however, there were no side reactions due to the functional groups in the capping agents. Thus, the inertness of methyl hydroxyacetate probably results from the electron-withdrawing α-carbonyl that substantially reduces the basicity of the hydroxyl group.

Consequently, it was decided to employ a series of β-substituted ethanol derivatives as primary alcoholic capping agents. Thus, the HI/ZnI_2-initiated living poly(pMOS) was terminated with three kinds of 2-hydroxyethyl carboxylates: acetate (**7a**), methacrylate (**7b**), and acrylate (**7c**). All polymers showed very narrow MWDs ($\overline{M}_w/\overline{M}_n < 1.1$; Table III).

Figure 3 shows the ^{1}H NMR spectra of these polymers. For example, a typical spectrum of the polymer obtained with **7a** is given in Figure 3A. All key absorptions of both "head" methyl (peak c) and "tail" acetoxy (peaks d and g) groups are seen, confirming the structure expected for polymer **8a**. The ratio of the "head" methyl protons (peak c) to the main-chain methoxy or phenyl protons (a/c or b/c) gave the observed $\overline{DP}_n$, which proved almost equal to the value calculated from the pMOS/HI (initiator) feed ratio. The $\overline{F}_n$ of **8a** was obtained from the ratio of the "head" methyl protons to the methylene protons of the "tail" oxyethyl acetate group (d/c) and was almost equal to unity (Table III, entry 11).

Very similar results were obtained for the polymers prepared by the end-capping with other functional primary alcohols (**7b** and **7c**). Quantitative formation of polymers **8b** (methacryloxy-end) and **8c** (acryloxy-end) were confirmed by ^{1}H NMR analysis (Figures 3B and 3C); the $\overline{F}_n$'s were all close to unity (Table III, entry 12 and 13). These facts indicate that end-functionalized poly(pMOS) can be synthesized not only by the functional initiator method [Eq (1)] but by the end-capping method [Eq (2)] as well.

Living cationic polymers of vinyl ethers (CH_2=CH-OR) can be terminated by some alcohols (R'OH) quantitatively to give an alkoxy-capped polymer,[3] but the resulting end group is an acetal [~~CH(OR)(OR')] which is chemically unstable under acidic conditions. In contrast, for poly(alkoxystyrene)s, quenching with an alcohol leads to a chemically stable alkoxy end (ω-end), and this in turn permits

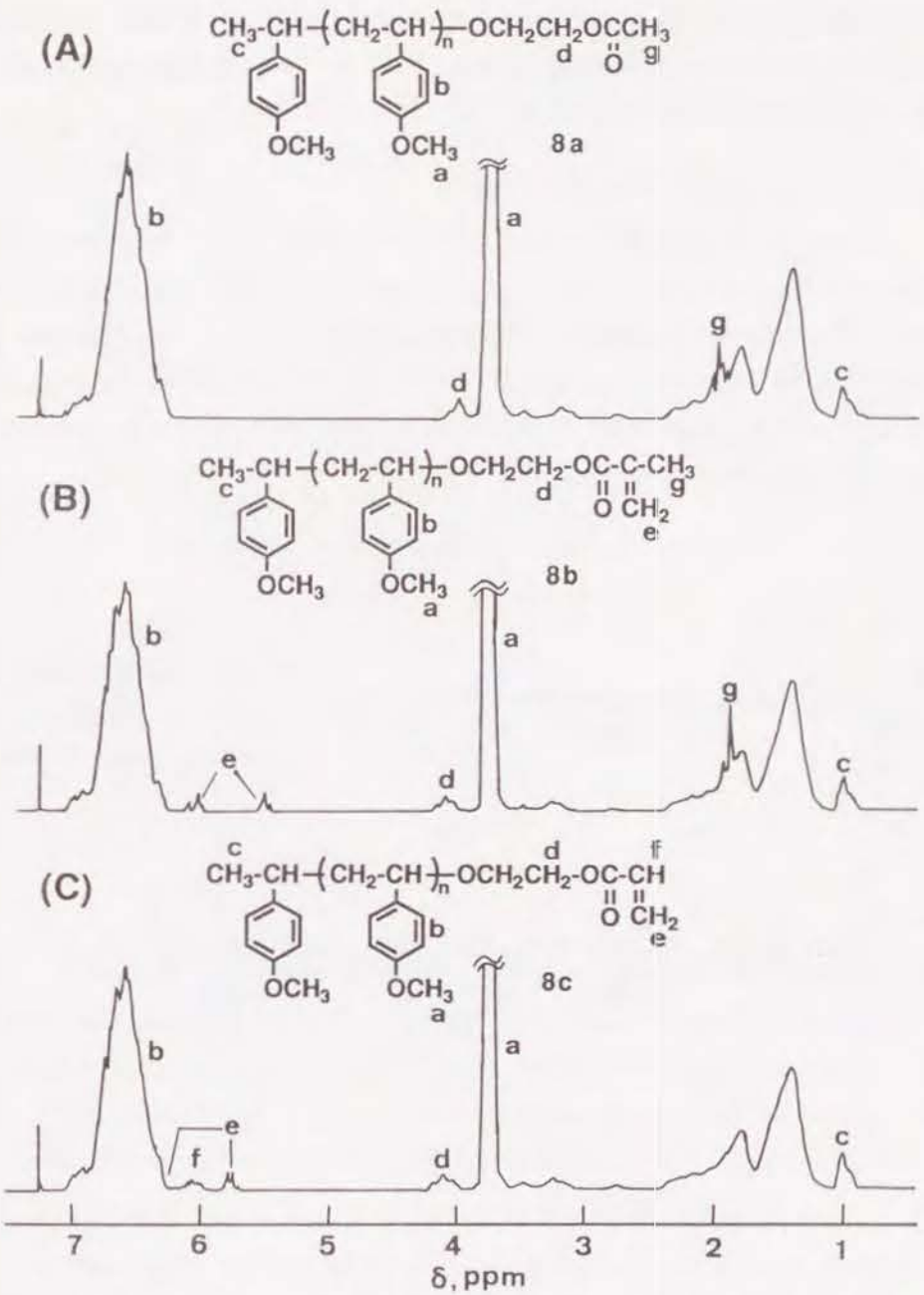
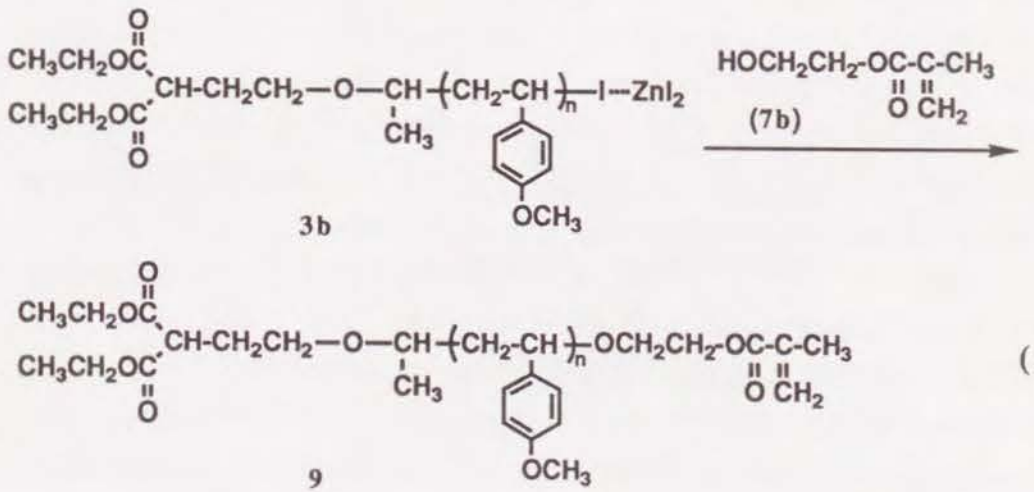


Figure 3. ^{1}H NMR spectra of end-functionalized poly(pMOS) (**8**): (A) acetoxy-capped, **8a**; (B) methacryloxy-capped, **8b**; (C) acryloxy-capped,**8c**; see entry 11 – 13, Table III.

the synthesis of poly(pMOS) with a variety of end-functional groups. In particular, **8b** and **8c** are new macromonomers with an anionically and radically polymerizable (meth)acryloxy group.

3. Hetero-Telechelic Poly(pMOS)

As applied to poly(vinyl ether)s,[4b] combination of the functional initiator method and the end-capping method, i.e., quenching the living polymer with alcohol **7**, led to hetero-telechelic polymers of pMOS [Eq (3)]. For example, living poly(pMOS) **3b** was prepared with the **2b**/ZnI_2 initiating system [Eq (1)], and its living end was subsequently end-capped in situ with excess 2-hydroxyethyl methacrylate (**7b**) to give polymer **9**.



(3)

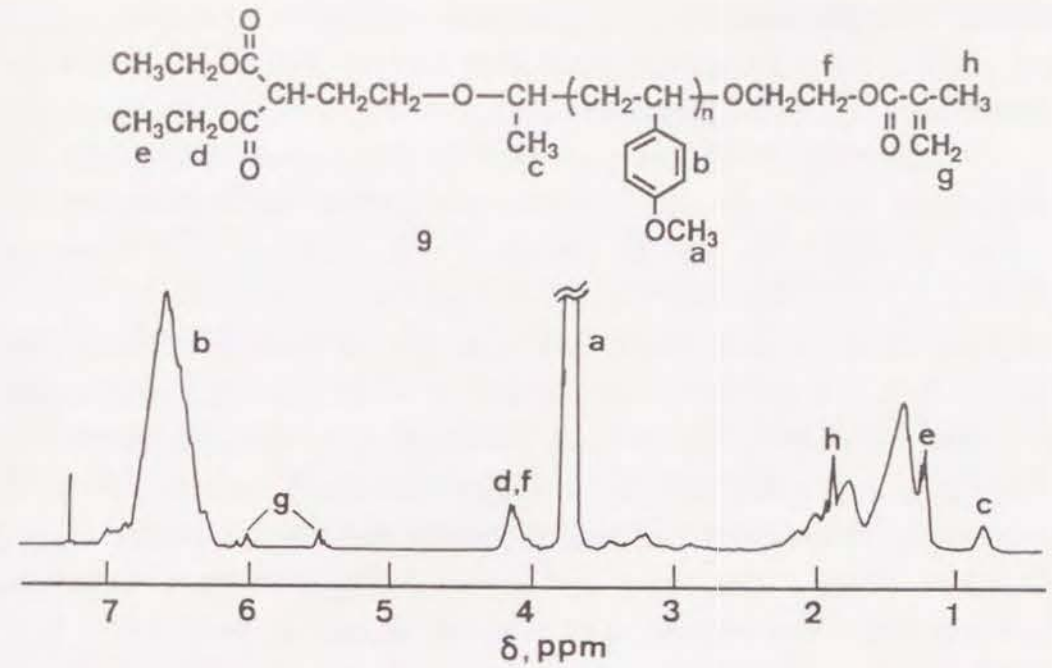


Figure 4. ^{1}H NMR spectrum of malonate-methacryloxy hetero-telechelic poly(pMOS) **9**.

The hetero-telechelic structure (**9**) of the products was established by ^{1}H NMR spectroscopy (Figure 4). The spectrum exhibits absorptions of the "head" ethyl malonate (peak d and e) and the "tail" methacrylate (peaks f – h) protons. The ratio of the "head" methyl protons (peak c) to the main-chain protons (a/c or b/c) gave $\overline{DP}_n$, which was almost equal to the calculated value [e. g., obd: 21.2 (from a/c), 21.4 (from b/c); calcd: 21.1 ($\bar{M}_n$= 2600, $\bar{M}_w/\bar{M}_n$= 1.08)].

The number-average end-functionalities $\overline{F}_n$ were determined from the peak intensity ratio of the "head" malonate (peak d) and the "tail" methacrylate groups (peak g) to the initial methyl group arising from the initiator (peak c): $\overline{F}_n(\alpha)$ = d/c (for the malonate end); $\overline{F}_n(\omega)$ = g/c (for the methacrylate end). Both $\overline{F}_n(\alpha)$ (= 0.99) and $\overline{F}_n(\omega)$ (= 1.01) are close to unity, indicating the quantitative attachment of one malonate and one methacrylate groups per polymer **9**.

EXPERIMENTAL

Materials

Commercial pMOS (Fluka) was washed with an aqueous alkali solution and then water, dried overnight over anhydrous sodium sulfate, and distilled twice over calcium hydride under reduced pressure. Functionalized vinyl ethers [2-acetoxyethyl vinyl ether (**1a**),[15] diethyl 2-vinyloxyethyl malonate (**1b**),[16] and 2-vinyloxyethyl phthalimide (**1c**)[3]] were synthesized as reported, and these were purified by double distillation over calcium hydride under reduced pressure. The gas-chromatographic purity of those monomers were all exceeded 99.8 %. Capping agents [2-hydroxyethyl acetate (**7a**), 2-hydroxyethyl methacrylate (**7b**), 2-hydroxyethyl acrylate (**7c**), methanol, isopropanol and *t*-butanol; all from Wako Chemicals, purity > 99%] were used without further purification. Anhydrous hydrogen iodide was prepared as an *n*-hexane solution as described.[17] ZnI_2 (Aldrich, purity > 99.99%) was used as received; it was vacuum dried overnight just before use and handled in the dark under dry nitrogen.[18] Toluene (polymerization solvent), diethyl ether (solvent for ZnI_2) and tetrahydronaphtalene (internal standard for gas chromatography) were purified by the usual methods[7] and distilled twice over calcium hydride just before use.

Procedures

Polymerizations were carried out under dry nitrogen in a baked glass vessel equipped with a three-way stopcock.[4] When adduct **2** was used as an initiator, vinyl ether **1** was first treated with an equimolar amount of hydrogen iodide in *n*-hexane at -78°C. To this solution of **2** were added pMOS monomer and a ZnI_2 solution in this order, and after kept at the same temperature for 20h, the mixture was transferred to a methanol bath kept at -15°C to initiate polymerization. When hydrogen iodide was used as an initiator, precooled solutions of this acid (in *n*-hexane) and zinc iodide (in diethyl ether) were added successively in this order to a monomer solution (in toluene).[19] The living polymerizations were terminated by adding prechilled ammoniacal methanol or capping agents (see Tables I - III).

The quenched reaction mixtures were sequentially washed with 10% aqueous sodium thiosulfate solution and with water, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers. pMOS conversion was determined from its residual concentration measured by gas chromatography with tetrahydronaphthalene as an internal standard.

Polymer Characterization

The structure and the $\overline{DP}_n$ of the polymers were determined by ^1H NMR spectroscopy (270 MHz) at +40°C in $CDCl_3$ on a JEOL GSX-270 spectrometer (see Results and Discussion). The MWD of the products was determined by size-exclusion chromatography in chloroform at room temperature on a Jasco Trirotar chromatograph equipped with polystyrene gel columns (Shodex K-802, K-803 and K-804; 8.0mm i.d. × 300mm each) and reflux index/ultraviolet dual detectors. The polydipersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from size-exclusion eluograms on the basis of a polystyrene calibration.

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20. The methoxy absorption (c) is split into two siglets due to the stereoisomerism of the terminal methine carbon to which it is attached.

CHAPTER 4

END-FUNCTIONALIZED POLYMERS OF *p-t*-BUTOXYSTYRENE

ABSTRACT

A series of end-functionalized polymers of *p-t*-butoxystyrene (tBOS), with an acetoxy, ethyl malonate, or methacryloxy terminal, were synthesized by living cationic polymerization with the hydrogen iodide/zinc iodide (HI/ZnI_2) initiating system:

$X\text{-}CH_2CH_2OCH(CH_3)(tBOS)_nOCH_3$ (**4**)
[X: $(C_2H_5OCO)_2CH$- (**4a**); CH_3COO- (**4b**)];
$H\text{-}(tBOS)_nOCH_2CH_2\text{-}Z$ (**8**)
[Z: $-OCOC(CH_3)=CH_2$ (**8a**), $-OCOCH_3$ (**8b**)]

For the synthesis of these polymers, the following two methods were employed: (1) for α-end functional polymer **4**, living polymerization of tBOS initiated with a functional vinyl ether-hydrogen iodide adduct **2** [X-$CH_2CH_2OCH(CH_3)$-I] in conjunction with ZnI_2; and (2) for ω-end functional polymer **8**, quenching the HI/ZnI_2-initiating living poly(tBOS) with a functional alcohol **7** [HO-CH_2CH_2-Z]. All these polymers were shown to possess controlled molecular weights ($\overline{DP}_n = [tBOS]_0/[initiator]_0$), very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$), and end-functionalities close to unity. The endgroups of polymers **4a** and **4b** could be converted into carboxy (**5a**) and hydroxy (**5b**) functions, respectively.

$Y\text{-}CH_2CH_2OCH(CH_3)(tBOS)_nOCH_3$ (**5**)
[Y: $HOOCCH_2$- (**5a**); HO- (**5b**)];

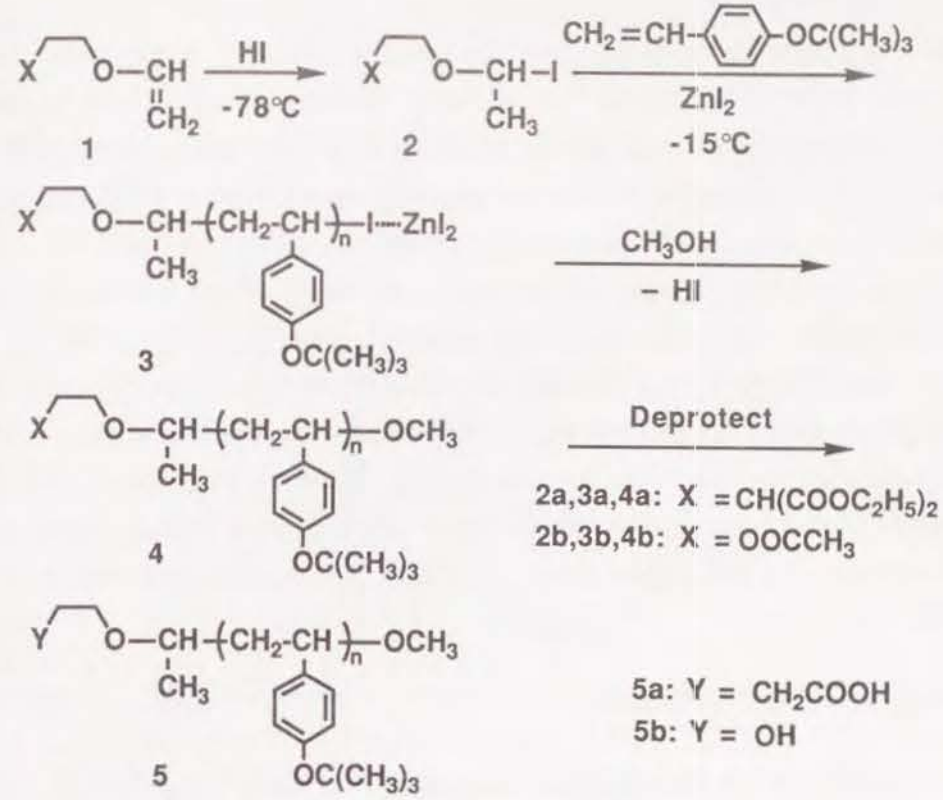
INTRODUCTION

As a pendant-functionalized *p*-alkoxystyrene, *p*-*t*-butoxystyrene (tBOS) is of interest in that treatment of its polymer with an acid leads to poly(*p*-hydroxystyrene), which finds a wide variety of applications to photoresists, curing agents, adhesives, etc.[1] As Higashimura et al. have recently reported, tBOS[2] and its simpler analogue, *p*-methoxystyrene (pMOS),[3] can undergo living cationic polymerization with use of the hydrogen iodide/zinc iodide (HI/ZnI_2) initiating system. The preceding chapter of this thesis[4] concerns end-functionalized polymers of pMOS.

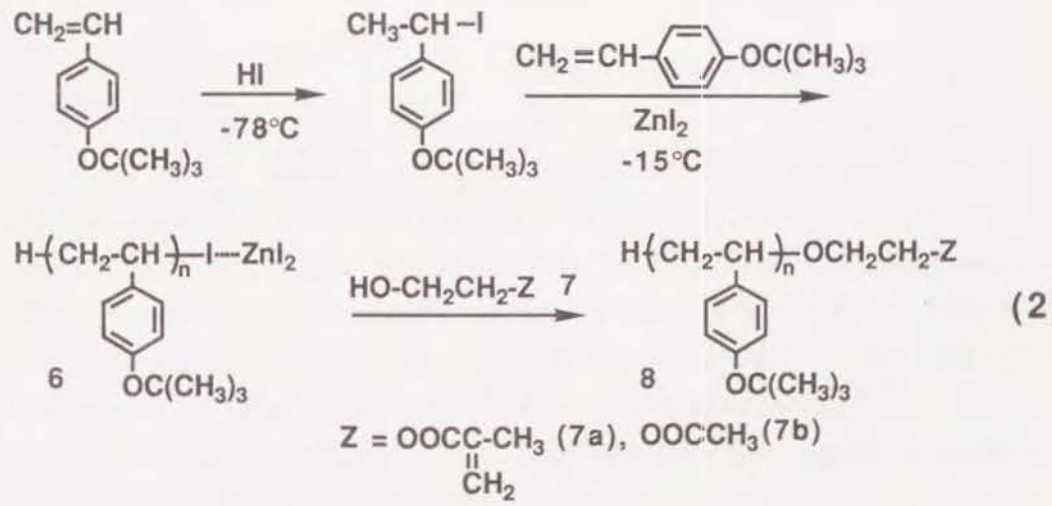
This chapter is now directed to extending these findings to tBOS in preparing another series of end-functionalized polymers from the pendant-functionalized *p*-alkoxystyrene, as outlined in Eq (1) and (2). Thus, similar to that for pMOS,[4] Eq (1) shows a "functional initiator method" that involves living cationic polymerization of tBOS initiated by a functional initiator (**2**) coupled with ZnI_2 activator; herein initiator **2** is an adduct of hydrogen iodide with a vinyl ether (**1**) carrying a functional group X. Provided that the polymerization with **2**/ZnI_2 is living, each α-end of the resulting polymers (**3**) carries a functional group attached to the initiators residue. On the other hand, Eq (2) illustrates an "end-capping method" where the HI/ZnI_2-initiated living polymer (**6**) of tBOS is terminated with a series of alcohols (**7**) that possess a functional group Y.

Despite the structural similarity to pMOS, tBOS is clearly less reactive than the methoxy derivative in living cationic polymerization, most probably because of the less electron-donating power of the sterically hindered *t*-butoxy group relative to the methoxy counterpart, as indicated by the ^{13}C NMR analysis of these monomers.[2,3] The same difference between the two alkoxy groups also suggests that the growing carbocation derived from tBOS is less stable than that from pMOS.

In view of these potential drawbacks, the application of the proposed end-functionalization methods [Eq (1) and (2)] to tBOS may not be straightforward, although both methods are perfectly feasible to pMOS.[4] In one hand, for example,



(1)



(2)

the key to the success of the functional initiator method lies in the clean and quantitative initiation by the vinyl ether-type initiator **2**, but this is not certain for less reactive monomers like tBOS. The success of the end-capping method, on the other hand, requires the absence of side-reactions during the end-capping of the HI/ZnI_2-generated living ends, but the less stable carbocation (**6**) of tBOS may be more susceptible to some undesirable reactions with basic quenchers like **7**.

Herein the author discusses the synthesis of a series of end-functionalized poly(tBOS) (**4**, **5**, and **8**) by the functional initiator method [Eq (1)] and the end-capping method [Eq (2)]. For the former, the functional initiators (**2**) carry a malonate (**2a**) or acetate group (**2b**), which, respectively, leads to a carboxylic acid or alcohol function; for the latter, the end-capping agents are alcohols (**7**) with a methacrylate (**7a**) or acetate (**7b**), which, respectively, gives a polymerizable or alcoholic terminal. As pointed out above, the results are also compared with those for pMOS.

RESULTS AND DISCUSSION

1. End-Functionalized Poly(tBOS) by Functional Initiator Method

As illustrated in Eq (1), a series of end-functionalized poly(tBOS) (**4**) were prepared with use of functional initiator **2**, which was the adduct of hydrogen iodide with vinyl ether **1**.

1-1. Living Cationic Polymerization

First, it was examined whether the vinyl ether-type initiating species from **2** can indeed induce a living cationic polymerization of tBOS. Thus, tBOS was polymerized in toluene at -15°C with **2a** in conjunction with ZnI_2, and the polymerization was also compared with that of pMOS under the same reaction conditions. As shown in the time-conversion curves in Figure 1, the vinyl ether cation (**2**) smoothly initiated both pMOS and tBOS polymerizations that were quantitative and free of an induction phase. Under these conditions, as expected, tBOS is polymerized slower than pMOS.

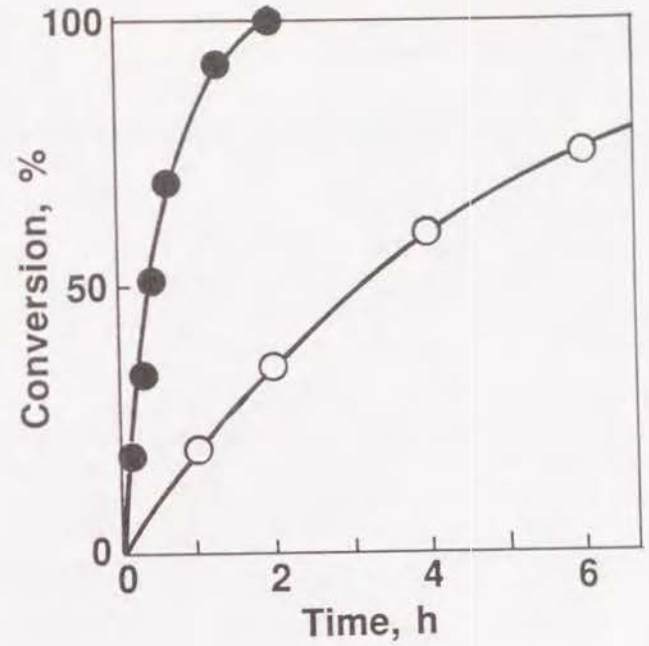


Figure 1. Time-conversion curves for the polymerizations of tBOS (O) and pMOS(●) obtained with $(C_2H_5OCO)_2CHCH_2CH_2OCH(CH_3)I$ (**2a**)/ZnI_2 initiating systems in toluene at -15°C: $[tBOS]_0 = [pMOS]_0 =$ 0.50 M; $[\mathbf{2a}]_0$ = 10 mM; $[ZnI_2]_0$ = 5.0 mM.

Figure 2 shows the number-average molecular weight ($\bar{M}_n$), polydispersity ratio ($\bar{M}_w/\bar{M}_n$), and molecular weight distribution (MWD) for the poly(tBOS) obtained at three concentrations of initiator **2a** ($[tBOS]_0$, constant; conversion ~ 100%). The MWDs of the polymers were very narrow and shifted toward higher molecular weight as the monomer/**2a** ratio increased; the $\bar{M}_w/\bar{M}_n$ ratio remained unchanged and well below 1.1. The $\bar{M}_n$'s of the polymers increased in direct proportion to the monomer/**2a** ratio. Separate experiments showed that the $\bar{M}_n$ of the polymers increased in direct proportion to monomer conversion. These facts show the living nature of the polymerization of tBOS initiated with the **2a**/ZnI_2 system, although the monomer is not as reactive as pMOS.

Similar results were obtained for polymerization of tBOS with another functional initiator **2b** carrying an acetoxy pendant group.

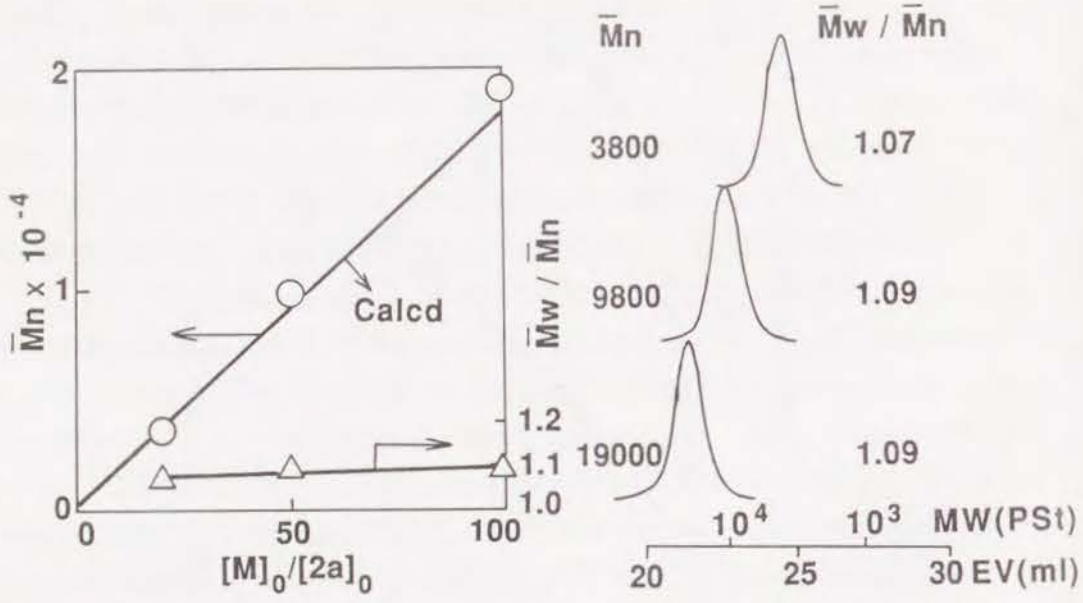


Figure 2. $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and MWD of poly(tBOS) obtained with $(C_2H_5OCO)_2CHCH_2CH_2OCH(CH_3)I$ (**2a**)/ZnI_2 (eq. 1) in toluene at −15°C at three initiator (**2a**) concentrations: $[tBOS]_0$ = 0.50 mM; $[\mathbf{2a}]_0$ = 5, 10, and 20 mM; $[ZnI_2]_0$ = 5.0 mM; conversion ~ 100%.

1-2. Polymer Characterization.

The endgroup structure of the polymers (**4a**) was determined by ^1H NMR spectroscopy. Figure 3A depicts the ^1H NMR spectrum of a typical sample obtained with **2a**/ZnI_2. The spectrum exhibits all key absorptions of the poly(tBOS) main chain (a and f), the malonate group of the initiator fragment (c), and the methoxy terminal (b) derived from termination with methanol. All these observations are consistent with structure **4a**.

The number-average degree of polymerization ($\overline{DP}_n$) for **4a** was determined from the intensity ratio of the pendant phenyl groups to the terminal methoxy (a/b); it has been shown that quenching living ends like **3** with excess methanol is quantitative and clean to give a methoxy terminal. As shown in Table I, $\overline{DP}_n$'s were in good agreement with the calculated values (= $[tBOS]_0/[\mathbf{2a}]_0$) with theassumption that each molecule of initiator **2a** generates one living chain.

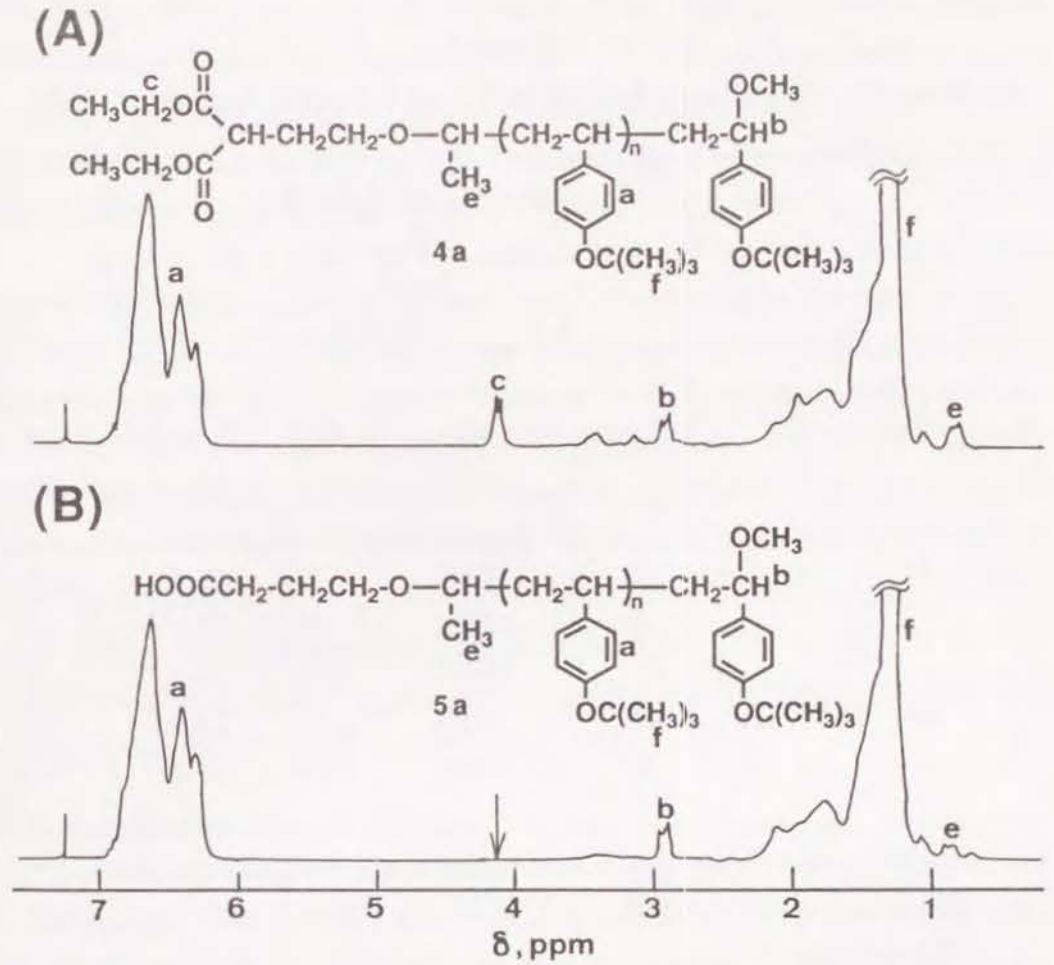
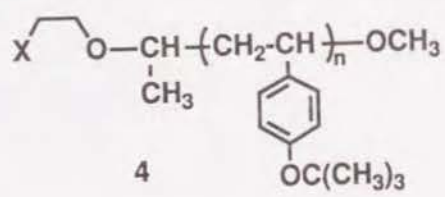


Figure 3. ^1H NMR spectra: (A) malonate-capped poly(tBOS) **4a** (sample 1, Table I); (B) carboxy-capped poly(tBOS) **5a** from sample 1.

Table I

Synthesis of End-Functionalized Poly(tBOS) with Functional Initiator Method[a]



4

Entry	Code	X[a]	$\overline{DP}_n$(calcd)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$\overline{DP}_n$(obd)[d,e] a/b	$\bar{F}_n$[d,f] c/b
1	**4a**	$CH(COOEt)_2$	20	3800	1.07	20.3	0.98
2			50	10700	1.09	52.0	1.00
3			100	19000	1.09	104.0	1.02
4	**4b**	$OOCCH_3$	20	3600	1.09	20.4	1.00
5			50	9500	1.09	52.0	0.99

a) Polymerizations were carried out in toluene at -78°C (20h) and then -15°C to 100 % conversion. $[tBOS]_0 = 0.50$ M; $[\mathbf{2}]_0 = 5 - 25$ mM; $[ZnI_2]_0 = 2.5 - 12.5$ mM.

b) $\overline{DP}_n$ (calcd) = $[tBOS]_0/[\mathbf{2}]_0$.

c) Measured by size-exclusion chromatography.

d) Based on the indicated ^1H NMR peak intensity ratio; see Figures 2 and 3.

e) Number-average degree of polymerization.

f) Number-average end functionality.

The number-average end-functionality ($\bar{F}_n$) of the terminal (α-end) malonate for **4a** was determined by comparing the integrated ^1H NMR peak areas of the esters methylene (c) with that of the ω-end methoxy group (b) (ratio: c/b). $\bar{F}_n$ was invariably close to unity, indicating the formation of malonate-capped poly(pMOS) **4a** that has exactly one malonate group per chain (Table I, entry 1–3).

Very similar results were obtained for the polymers (**4b**) synthesized with initiator **2b**, which carries an acetoxy group. The ^1H NMR spectrum of **4b** is shown in Figure 4A. All key absorptions of the polymer main chain (a and f) and the acetoxy group from the initiator fragment (c and d) are seen, all of which are consistent with the expected structure of polymer **4b**. The $\overline{DP}_n$ for **4b** was determined from the peak intensity ratio of the pendant phenyl groups to the terminal methoxy (a/b). The observed $\overline{DP}_n$'s were in good agreement with the $[tBOS]_0/[\mathbf{2b}]_0$ ratios. The $\bar{F}_n$ for **4b** was determined by comparing the ^1H NMR peak areas of the α-end acetoxy and the ω-end methoxy (c/b). The $\bar{F}_n$ was close to unity, indicating the formation of acetoxy-capped poly(tBOS) **4b** with exactly one acetoxy group per chain. (Table I, entry 4 and 5).

1-3. End-Group Transformation

As shown in Eq (1), the terminal functional groups of the polymers **4a** and **4b** were converted into the corresponding carboxy (**5a**) and hydroxy (**5b**) terminals, respectively. For example, a sample of **4a** (Table I, entry 1) was subjected to alkaline hydrolysis, followed by thermal decarboxylation, to give its carboxy-capped version **5a** (Figure 3B). The signal associated with the malonate terminal (4.20 ppm; see Figure 3A, peak c) is absent in the hydrolysis/decarboxylation product, indicating the formation of the carboxy-capped poly(tBOS) **5a**. The structure, $\overline{DP}_n$, and MWD of the poly(tBOS) backbone remained unchanged during the end-group transformation.

In a similar manner, the α-end acetoxy group of **4b** (Table I, entry 4) was converted into the corresponding hydroxy group by the hydrolysis under mild alkaline conditions (Figure 4B). The signals due to the acetoxy terminal of **4b** (4.05 ppm; Figure 4A, peak c) is absent in Figure 4B, where the alcoholic proton of **5b** is in turn seen (3.50 ppm; peak c').

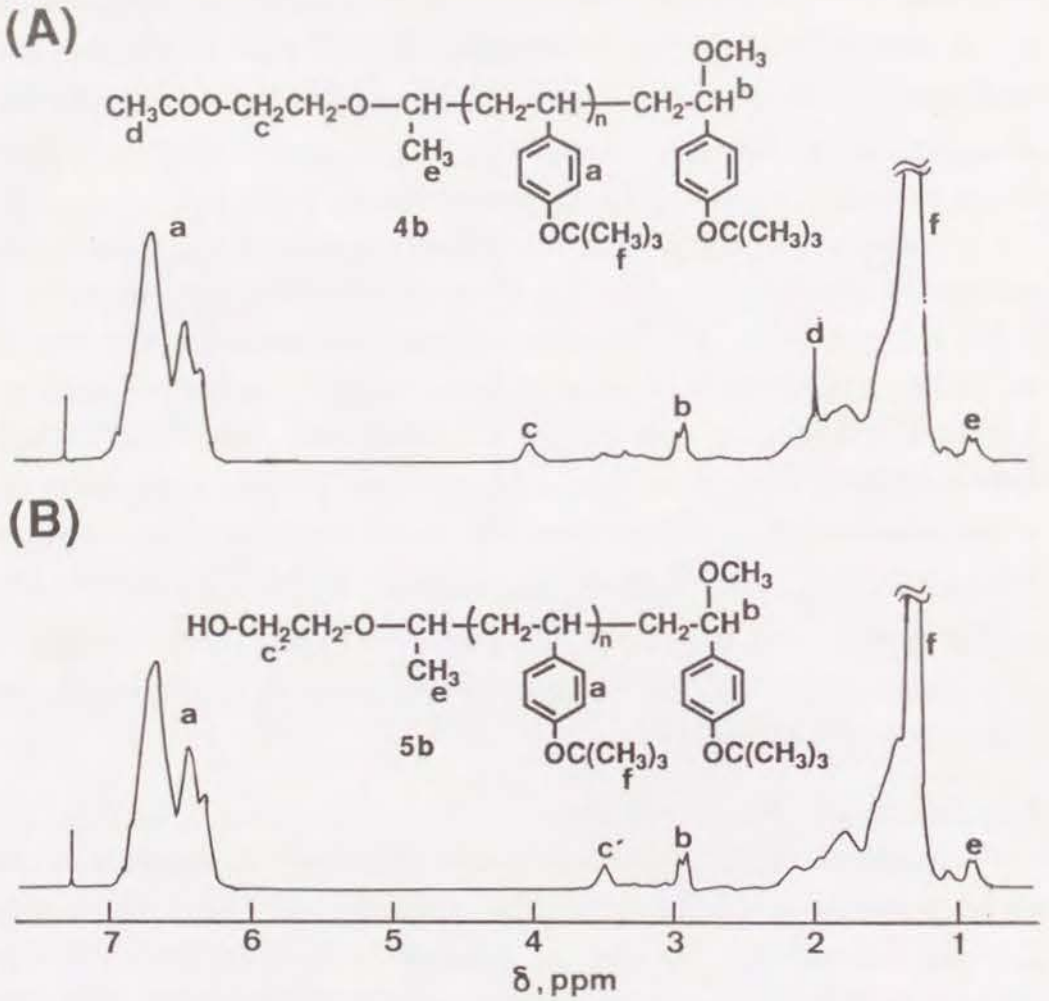


Figure 4. ^{1}H NMR spectra: (A) acetoxy-capped poly(tBOS) **4b** (sample 4, Table I); (B) hydroxy-capped poly(tBOS) **5b** from sample 4.

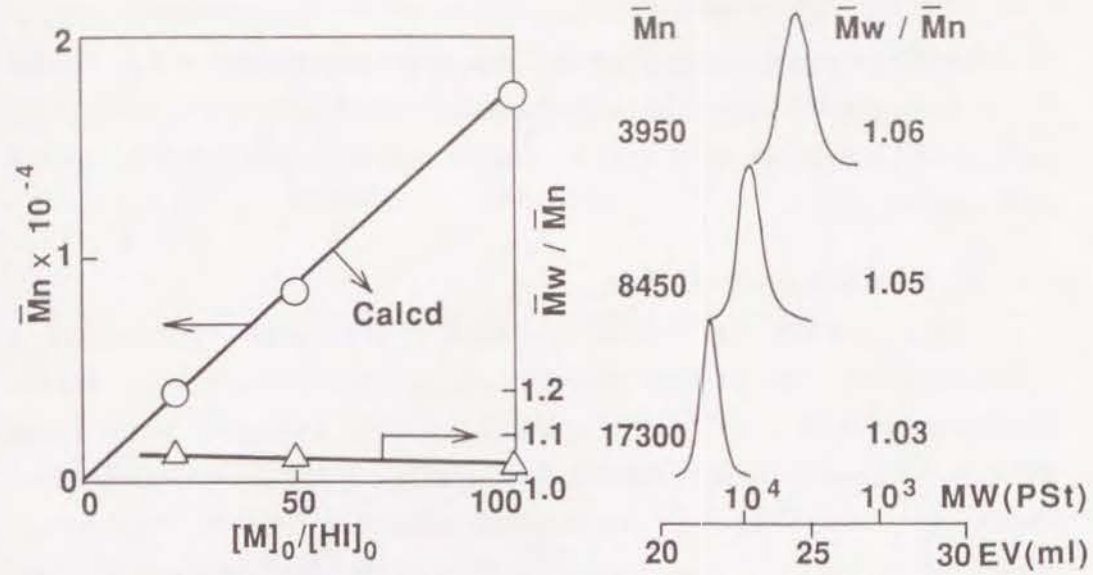


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of poly(tBOS) obtained [Eq (2)] in toluene at -15°C at three HI concentrations and terminated with 2-hydroxyethyl methacrylate (**7a**): $[tBOS]_0$ = 0.50 mM; $[HI]_0$ = 5, 10, and 23 mM; $[ZnI_2]_0$ = 5 mM; conversion ~ 100%.

2. End-Functionalized Poly(tBOS) by End-Capping Method.

2-1. End-Capping

End-functionalization of poly(tBOS) was also carried out by the end-capping method [Eq (2)]. As discussed in Chapter 3,[4] 2-hydroxyethyl carboxylates, as functional primary alcohols, react quantitatively with the living poly(pMOS) growing ends to give ester terminals. The author has decided to employ 2-hydroxyethyl methacrylate (**7a**) and 2-hydroxyethyl acetate (**7b**) as capping agents for living poly(tBOS) (**6**).

Thus, for example, living cationic polymerization of tBOS was carried out with the HI/ZnI_2 initiating system in toluene at -15°C, and near at 100% conversion, it was terminated with **7a** in a large molar excess over the living ends. Figure 5 shows the $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$ and MWD of the polymers obtained with three monomer/HI ratios.

The $\overline{M}$n's of the poly(tBOS) **8a** increased in direct proportion to the monomer/HI ratio, and the $\overline{M}$w/$\overline{M}$n ratios were invariably well below 1.1. Similar results were obtained for the polymers terminated with **7b** as capping agent. In all these cases, furthermore, there were no side reactions due to the functional groups in the capping agents.

2-2. Polymer Characterization

Figure 6 shows the ^{1}H NMR spectra of these polymers. For example, a typical spectrum of the polymer obtained with **7a** is given in Figure 6A. All key absorptions of both "head" methyl (peak g) and "tail" 2-oxyethyl methacrylate (peaks b – d) groups are seen, and absorptions assignable to other end groups were absent. The ratio of the "tail" methacryloxy protons to the main-chain phenyl protons (a/b or a/c) gave the observed $\overline{DP}_n$, which proved almost equal to the value calculated from the tBOS/HI feed ratio (Table II, entry 6 – 8).

Very similar results were obtained for the polymers prepared with **7b**. Quantitative formation of acetoxy-capped poly(tBOS) **8b** is confirmed by ^{1}H NMR analysis; the observed $\overline{DP}_n$'s of **8b** were close to the calculated values (Table II, entry 9 and 10).

In conclusion, despite the low reactivity of tBOS and the expected lower stability of the growing carbocation, a series of end-functionalized poly(tBOS) have been synthesized by the functional initiator method [Eq (1)] and the end-capping method [Eq (2)]. As applied to pMOS,[4] combination of the two methods will lead to homo- and hetero-telechelic polymers of tBOS.

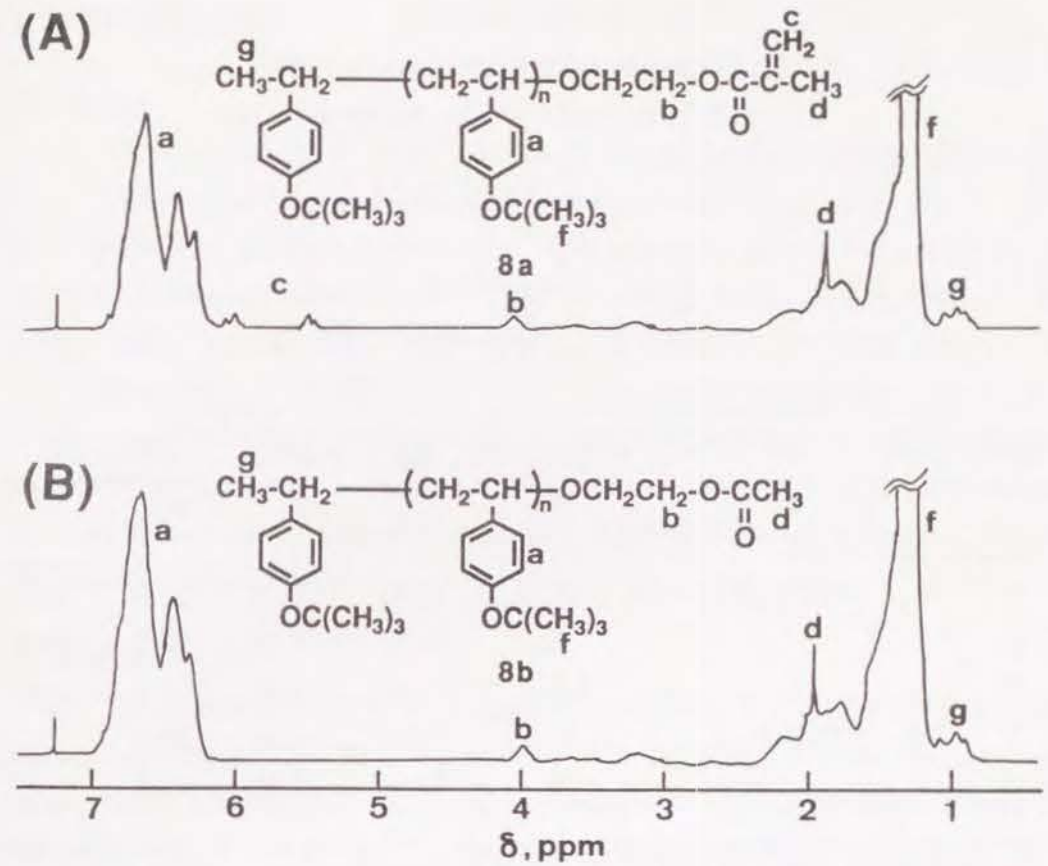
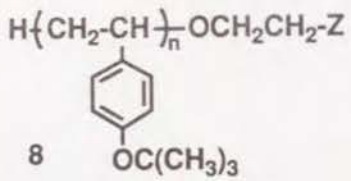


Figure 6. ^{1}H NMR spectra: (A) methacryloxy-capped poly(tBOS) **8a** (sample 6, Table II); (B) acetoxy-capped poly(tBOS) **8b** (sample 9, Table II).

Table II

Synthesis of End-Functionalized Poly(tBOS)
with Functional End-Capping Method[a]



Entry	Code	Z[a]	$\overline{DP}_n$(calcd)[b]	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	$\overline{DP}_n$(obd)[d]	
						a/b	a/c
6	**7a**	$OOCC(CH_3)=CH_2$	21.5	4000	1.06	21.9	21.9
7			50	8450	1.05	50.0	49.0
8			100	17300	1.03	103.0	101.0
9	**7b**	$OOCCH_3$	27.8	4751	1.06	28.3	
10			50	8220	1.05	51.8	

a) Polymerization by HI/ZnI_2 in toluene at -15°C; $[tBOS]_0 = 0.50$ M; $[HI]_0 = 5 - 23$ mM; $[ZnI_2]_0 = 2.5 - 12$ mM.

b) $\overline{DP}_n$ (calcd) = $[tBOS]_0/[HI]_0$.

c) Measured by size-exclusion chromatography.

d) Number-average degree of polymerization, based on the indicated ^1H NMR peak intensity ratio; see Figure 5.

EXPERIMENTAL

Materials

Commercial tBOS (Hokko Chemical) was purified as reported.[3] Diethyl 2-vinyloxyethyl malonate (**1a**)[5] and 2-acetoxyethyl vinyl ether (**1b**)[6] were synthesized and purified as described. The gas-chromatographic purity of the monomers all exceeded 99.8%. 2-Hydroxyethyl methacrylate (**7a**) and 2-hydroxyethyl acetate (**7b**) (Wako Chemicals, purity > 99%) and zinc iodide (Aldrich, purity > 99.999%) were used without further purification. Hydrogen iodide was obtained by dehydrating a commercial 57w/v% hydroiodic acid with phosphorous pentoxide.[5,7] Solvents (toluene and diethyl ether) and an internal standard for gas chromatography (tetrahydronaphthalene) were purified and used as described in the literature.[7]

Procedures

Polymerization of tBOS was carried out under nitrogen as described in the preceding chapter.[4] tBOS conversion was determined from its residual concentration measured by gas chromatography with tetrahydronaphthalene as an internal standard (2.5 vol%). The quenched reaction mixtures were washed with 10% aqueous sodium thiosulfate solution and then with water to remove initiator residues, evaporated to dryness below 40°C under reduced pressure, and vacuum dried to give the produced polymers. Deprotection of the produced polymers (**4a**[5] and **4b**[6]) was described.[4]

Polymer Characterization

MWD of the products was determined by size-exclusion chromatography (SEC) in chloroform at room temperature on a Jasco Trirotar chromatograph equipped with polystyrene gel columns (Shodex K-802, K-803 and K-804; 8.0 mm i.d. × 300mm each) and refractive index/ultraviolet dual detectors. The number-average molecular weight ($\overline{M}_n$) and polydispersity ratio ($\overline{M}_w/\overline{M}_n$) were calculated from SEC eluograms on the basis of a polystyrene calibration. ^1H NMR spectra (270MHz) were recorded at +40°C on a JEOL GSX-270 spectrometer in $CDCl_3$.

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PART 2

SYNTHESIS OF TRI-ARMED FUNCTIONAL POLYMERS BY LIVING CATIONIC POLYMERIZATION

CHAPTER 5

TRI-ARMED STAR POLYMERS OF ISOBUTYL VINYL ETHER BASED ON NOVEL TRIFUNCTIONAL INITIATORS

ABSTRACT

Tri-armed star polymers of isobutyl vinyl ether (IBVE) were synthesized by living cationic polymerization with a mixture of $EtAlCl_2$ and a new trifunctional initiator (**1** and **2**):

CH_3-C-[C_6H_4-OCH_2CH_2O-$CH(CH_3)OCOCF_3$ (*p*-)]$_3$ (**1**)
C_6H_3-[$COOCH_2CH_2O$-$CH(CH_3)OCOCF_3$]$_3$ (1,3,5-) (**2**)

at 0°C in the presence of 1,4-dioxane (an added base for carbocation stabilization). The tris(trifluoroacetate)-type initiators, **1** and **2**, were obtained from the corresponding trifunctional vinyl ethers. The number-average molecular weights ($\bar{M}_n$) of the polymers thus prepared increased in direct proportion to monomer coversion and were close to the calculated values assuming that each molecule of **1** or **2** produces one living chain; the molecular weight distribution (MWD) was very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the polymerizations. The generation of three living ends per molecule of **1** or **2** was confirmed by comparing the polymerization with that by its monofunctional analog (3 or 4, respectively):

C_6H_5-OCH_2CH_2O-$CH(CH_3)OCOCF_3$ (**3**)
C_6H_5-$COOCH_2CH_2O$-$CH(CH_3)$-$OCOCF_3$ (**4**)

as well as by end-capping analysis with sodiomalonic ester. When the ester-type core of the poly(IBVE) obtained with **2** was hydrolyzed under alkaline conditions, the $\bar{M}_n$ was reduced to one third with the narrow MWD unchanged, thus indicating that the polymer possesses exactly three arm chains with a uniform and controlled length.

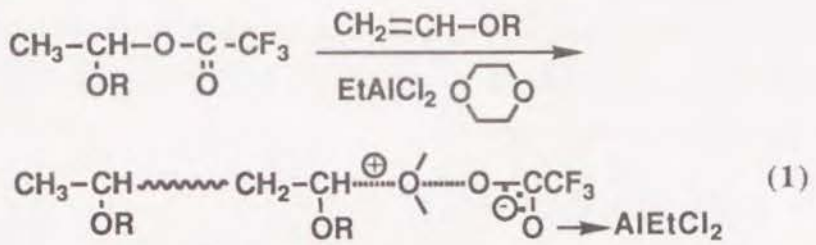
INTRODUCTION

Tri-armed star polymers are among advanced polymer materials that may find uses, for example, as crosslinking agents, ionomers, surface active agents, compatibilizers, prepolymers for elastomer etc. For their usefullness and versatility, they should satisfy at least two criteria: (i) the perfect end functionality (exactly three living ends per polymer molecule) and (ii) the controlled molecular weight and narrow molecular weight distribution (MWD) of each arm chain. These criteria may be achieved most readily by living polymerization with a trifunctional initiator.

Higashimura et al. have recently found living cationic polymerizations of vinyl ethers and styrene derivatives.[1] However, most of them are based on monofunctional initiators. Some trifunctional initiators have been developed by Kennedy et al., who obtained three-armed star polyisobutylenes via the inifer method[2] and living cationic polymerization.[3-7] However, these methods have been limited to nonpolar hydrocarbon monomers (isobutylene, etc.), and tri-armed polymers with functional pendant groups have not been obtained yet. In addition, all but one[8] studies have given no direct proof for the attachment of exactly three arms to a single core entity, as well as for their uniformity in length.

Part II of this thesis is concerned with the synthesis of tri-armed star polymers with controlled molecular weight, low polydispersity, and controlled arm lengths, via living cationic polymerization of vinyl ethers and *p*-alkoxystyrenes initiated by new trifunctional initiators. Another important objective is the synthesis of tri-armed star polymers with functional pendant groups, particularly from vinyl ethers, to which a variety of polar functions can readily be introduced without adversely affecting their living cationic polymerization.[9,10]

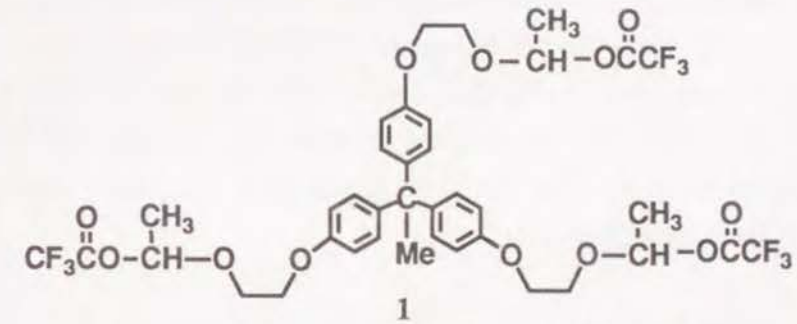
As reported previously,[11] living cationic polymerization of vinyl ethers may be initiated with a carboxylate adduct in conjunction with ethylaluminum dichloride ($EtAlCl_2$) and an excess amount of a weak Lewis base [Eq (1)]. The adduct is obtained from a vinyl ether and CF_3COOH, and with $EtAlCl_2$ its trifluoroacetate group initiates cationic polymerization of vinyl ethers in the presence of such a weak Lewis base as 1,4-dioxane, to generate living polymers, where the growing carbocation is stabilized by the added base.



(1)

Living Polymer

Based on this methodology, the author herein employed trifunctional compounds **1** and **2**, which were prepared from CF_3COOH and trifunctional vinyl ethers (**6** and **8**, respectively), as trifunctional initiators for living cationic



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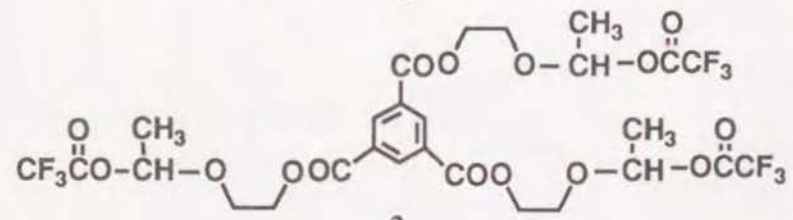

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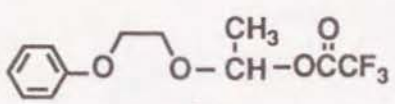

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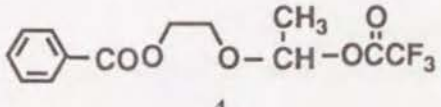

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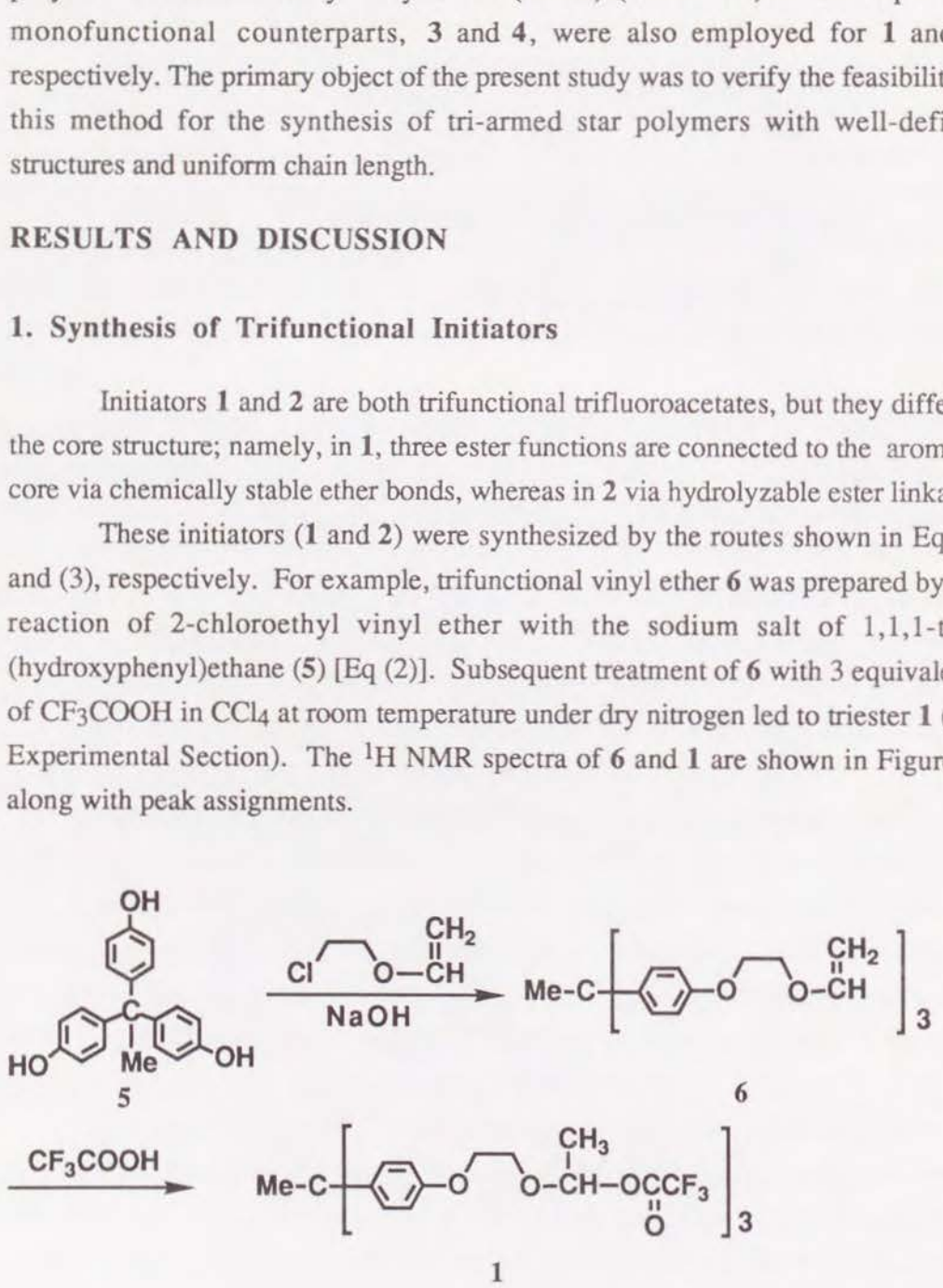
polymerization of isobutyl vinyl ether (IBVE) (see below). For comparison, monofunctional counterparts, **3** and **4**, were also employed for **1** and **2**, respectively. The primary object of the present study was to verify the feasibility of this method for the synthesis of tri-armed star polymers with well-defined structures and uniform chain length.

RESULTS AND DISCUSSION

1. Synthesis of Trifunctional Initiators

Initiators **1** and **2** are both trifunctional trifluoroacetates, but they differ in the core structure; namely, in **1**, three ester functions are connected to the aromatic core via chemically stable ether bonds, whereas in **2** via hydrolyzable ester linkage.

These initiators (**1** and **2**) were synthesized by the routes shown in Eq (2) and (3), respectively. For example, trifunctional vinyl ether **6** was prepared by the reaction of 2-chloroethyl vinyl ether with the sodium salt of 1,1,1-tris-(hydroxyphenyl)ethane (**5**) [Eq (2)]. Subsequent treatment of **6** with 3 equivalents of CF_3COOH in CCl_4 at room temperature under dry nitrogen led to triester **1** (see Experimental Section). The ^1H NMR spectra of **6** and **1** are shown in Figure 1, along with peak assignments.



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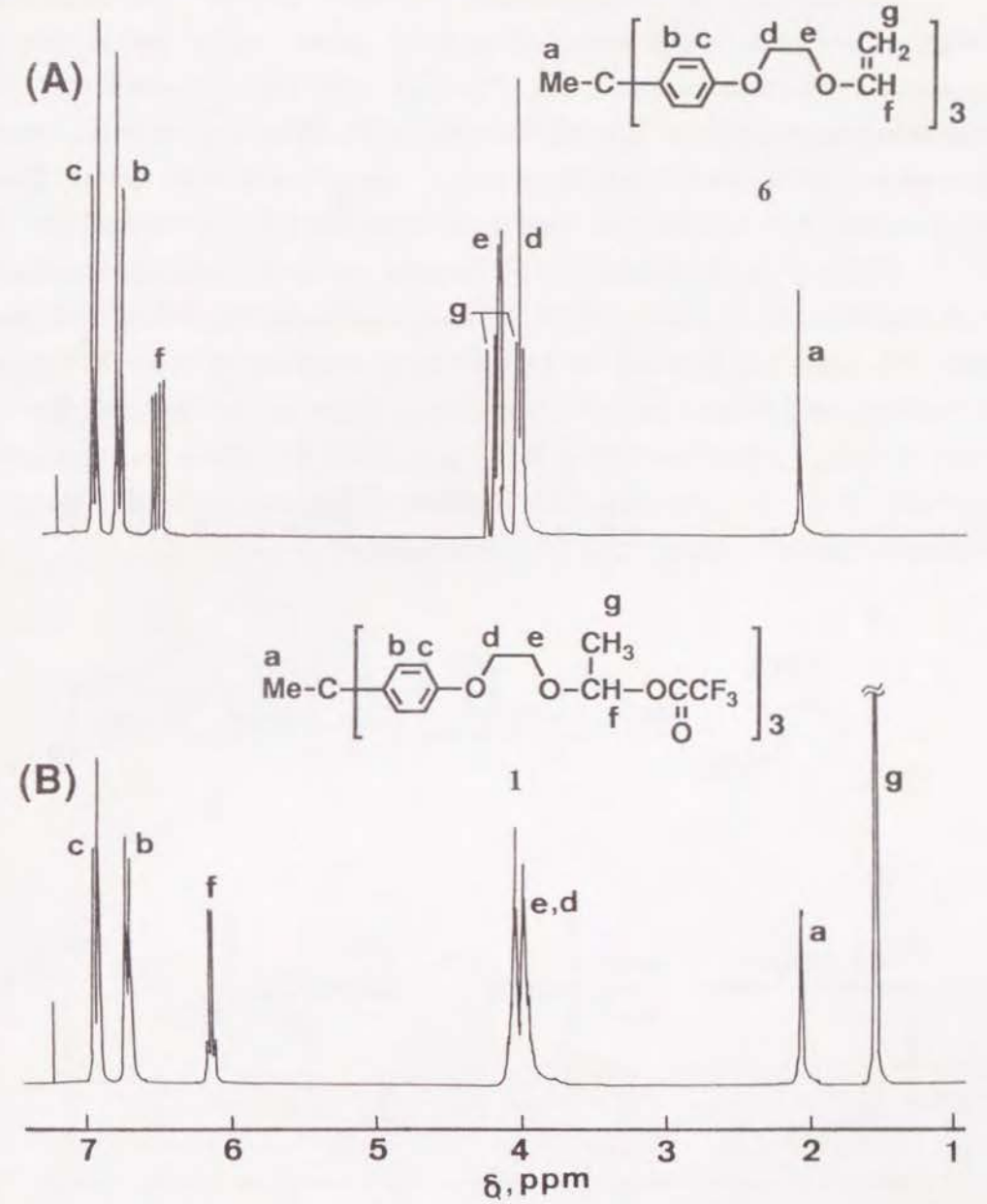
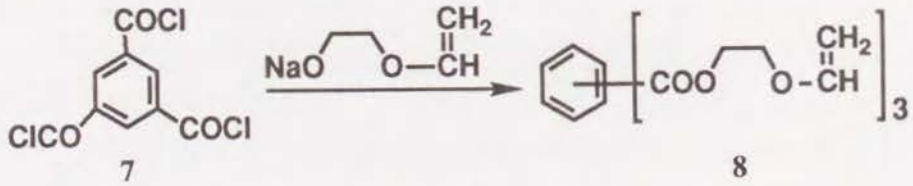


Figure 1. ^1H NMR spectra of (A) trivinyl ether **6** and (B) its trifluoroacetate form **1**.

The addition of CF_3COOH into a solution of **6** in CCl_4 caused the disappearance of the vinyl protons (Figure 1A, peaks f and g) and in turn the appearance of a quartet and a doublet (Figure 1B, peak f and g, respectively). The quartet is assignable to the -C*H*-$OCOCF_3$ group; the doublet is due to the methyl protons adjacent to the ester group. Signals of other products were absent. These NMR spectral data thus show the quantitative formation of trifunctional initiator **1**.

Similarly, as illustrated in Eq (3), the ester core-type trifunctional initiator **2** was obtained by the addition of CF_3COOH to the corresponding trifunctional vinyl ether (**8**), which was prapared by the reaction of trimessic chloride (**7**) with the sodium salt of 2-hydroxyethyl vinyl ether (see Experimental Section). The ^1H NMR spectra of **8** and **2** are shown in Figure 2, which also shows the quantitative formation of **2**. The solutions of the initiators **1** and **2** were directly employed without isolation for subseguent living polymerization.



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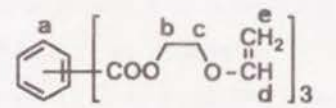

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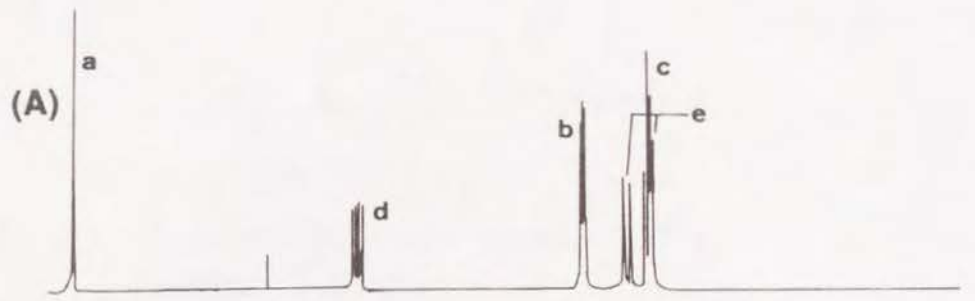

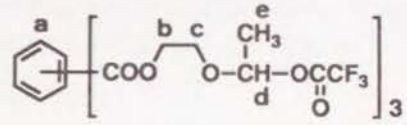

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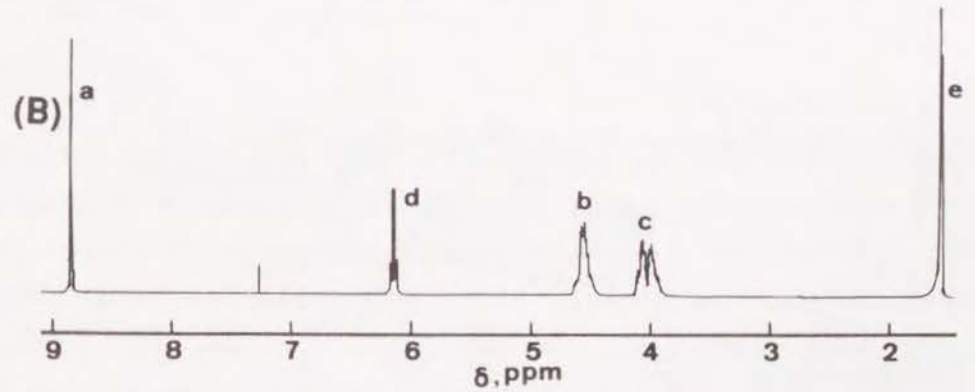
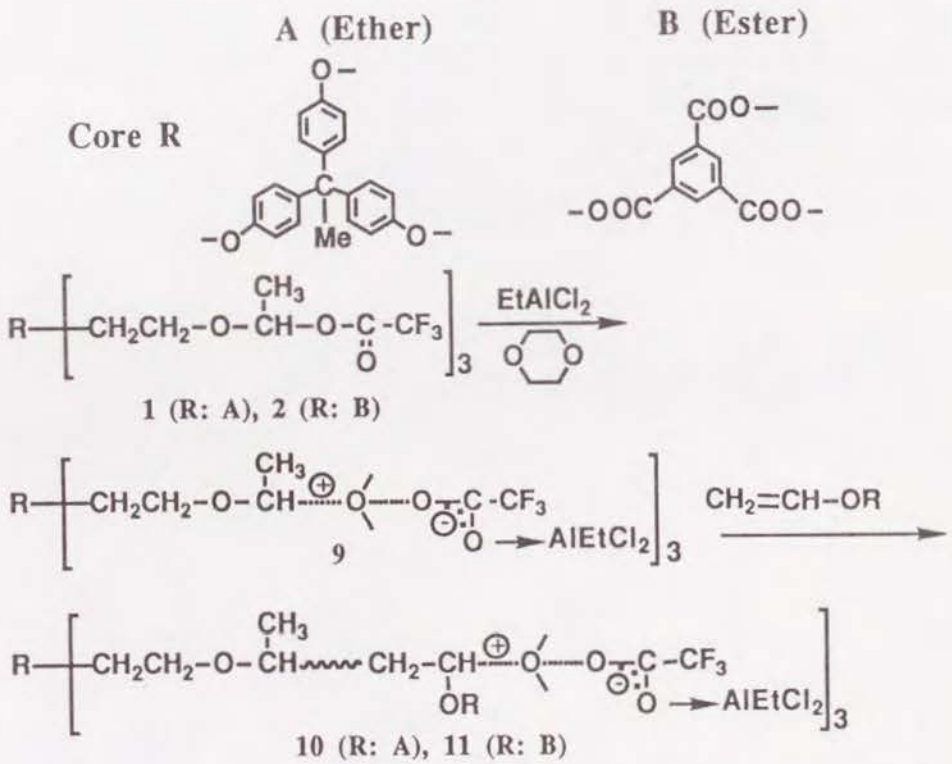


Figure 2. ^1H NMR spectra of (A) trivinyl ether **8** and (B) its trifluoroacetate form **2**.

2. Living Cationic Polymerization

Tri-armed star polymers were prepared via the general route illustrated in Scheme I, where the ether and ester cores of **1** and **2** designated as A and B, respectively. Thus, IBVE was polymerized in *n*-hexane at 0°C by **1** or **2**, coupled with $EtAlCl_2$ in the presence of 1,4-dioxane (10 vol% to the solvent). The polymerizations by **1** and **2** were first compared with those by the corresponding monofunctional analogs **3** and **4**, respectively.



Scheme I

2-1. Polymerization Rate

Figure 3 shows the time-conversion curves obtained with the two pairs of trifunctional and monofunctional initiators (Figure 3A for **1** and **3**; Figure 3B for **2** and **4**). When each of **1**-**4** alone was added to a monomer solution in the presence of 1,4-dioxane, virtually no polymer was formed in several hours, but the addition of $EtAlCl_2$ to this quiescent mixture effected a rapid polymerization that proceeded

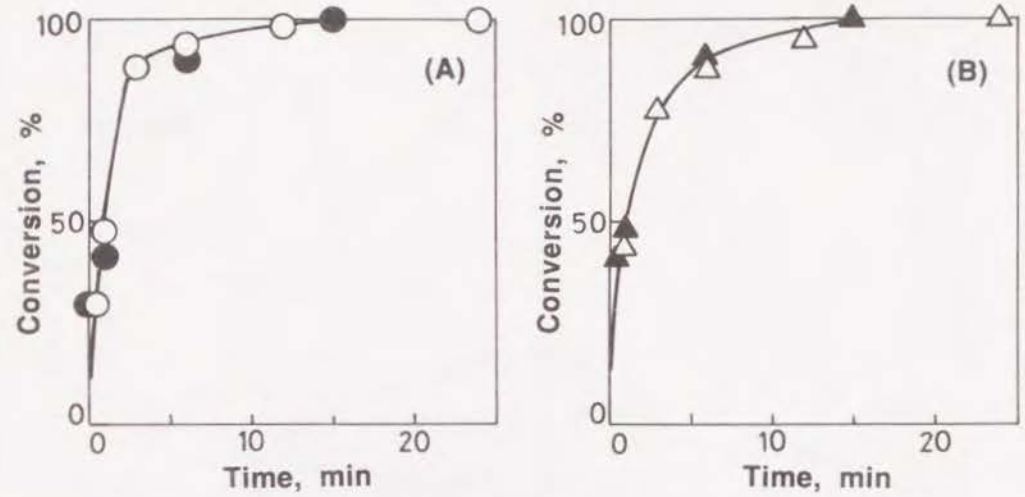


Figure 3. Time-conversion curves for the polymerization of IBVE with (A) trifunctional initiator (**1**) and monofunctional initiator (**3**) or (B) trifunctional initiator (**2**) and monofunctional initiator (**4**), coupled with $EtAlCl_2$ in *n*-hexane at 0°C; $[M]_0 = 0.76$ M, $[EtAlCl_2]_0 = 10$ mM, [1,4-dioxane] = 1.2 M. Initiator: (O) **1**, 3.5 mM; (●) **3**, 10 mM; (Δ) **2**, 3.5 mM; (▲) **4**, 10 mM.

quantitatively without an induction phase. When the initial concentrations of the trifluoroacetate functions (potential growing sites) were kept the same for the tri- and monofunctional initiators (10 mM; i.e., $[\mathbf{1}]_0 = 3.5$ mM and $[\mathbf{3}]_0 = 10$ mM; $[EtAlCl_2]_0 = 10$ mM), the polymerization rates with both initiating systems were in good agreement with each other (Figure 3A). Essentially the same results were obtained for the **2**/$EtAlCl_2$ (3.5/10 mM) and **4**/$EtAlCl_2$ (10/10 mM) initiating systems (Figure 3B). Therefore, each trifluoroacetate group of **1** and **2** can independently initiate IBVE polymerization in the presence of $EtAlCl_2$, and **1** or **2** gives the growing site at a concentration three times that from its monofunctional counterpart (**3** or **4**, respectively).

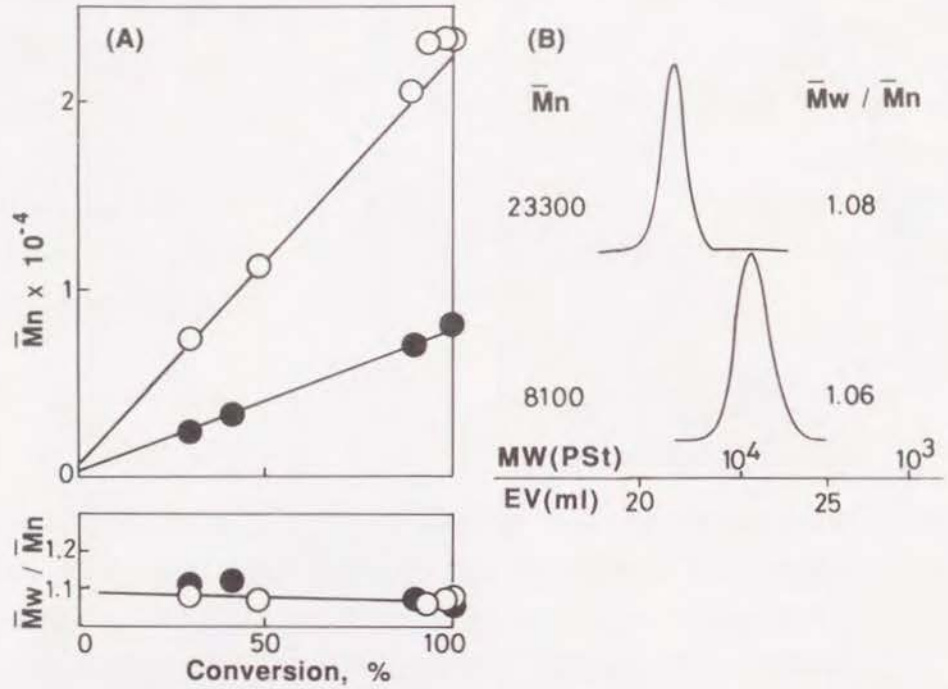


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$ and MWD of poly (IBVE) obtained with (a) trifunctional initiator **1**/$EtAlCl_2$ (**O**) and (b) monofunctional initiator **3**/$EtAlCl_2$ (●) in *n*-hexane at 0°C; the same experiments as for Figure 3(A). The intercepts in the $\bar{M}_n$-conversion plots show the molecular weights of the initiators (**1** and **3**).

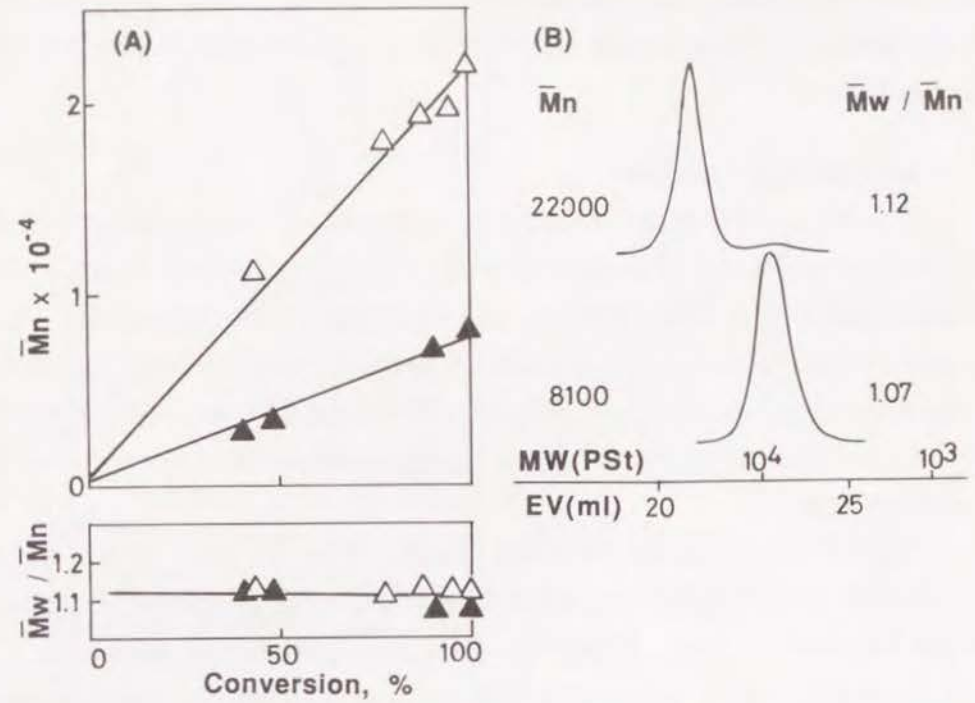


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$ and MWD of poly (IBVE) obtained with (c) trifunctional initiator **2**/$EtAlCl_2$ (Δ) and (d) monofunctional initiator **4**/$EtAlCl_2$ (▲) in *n*-hexane at 0°C; the same experiments as for Figure 3(B). The intercepts in the $\bar{M}_n$-conversion plots show the molecular weights of the initiators (**2** and **4**).

2-2. Polymer Molecular Weight and MWD

Figures 4 and 5 illustrate the number-average molecular weight ($\bar{M}_n$), polydispersity ratio ($\bar{M}_w/\bar{M}_n$), and MWD of the polymers obtained in the experiments shown in Figure 3. Regardless of the core structure (ether vs. ester) and functionality (tri- vs. monofunctional), all the four initiating systems led to living polymers, as shown by the linear increases in $\bar{M}_n$ against conversion (Figures 4A and 5A), as well as very narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$; Figure 4B and 5B).[12] However, the $\bar{M}_n$ values for the polymers obtained with the trifunctional initiators **1** and **2**, though based on a polystyrene calibration, were nearly three times those with the monofunctional counterparts **3** and **4**, respectively.

These facts show that trifunctional initiators **1** and **2** generate three living sites per molecule as in **10** and **11**, Scheme I, respectively. In addition to these MWD and relative $\bar{M}_n$ analysis by size-exclusion chromatography, the living nature of the polymerization with **1** or **2** were confirmed by determination of absolute $\bar{M}_n$ and end-functionality by ^1H NMR spectroscopy (see below).

The living polymers (**10** and **11**, Scheme I) were able to initiate polymerization again, when additional feeds of IBVE were added to reaction mixtures where the first IBVE doses had completely been polymerized. During

such "monomer-addition" experiments in *n*-hexane at 0°C, the $\overline{M}_n$ values increased in direct proportion to coversion and reached as high as 150,000 after the third monomer addition.

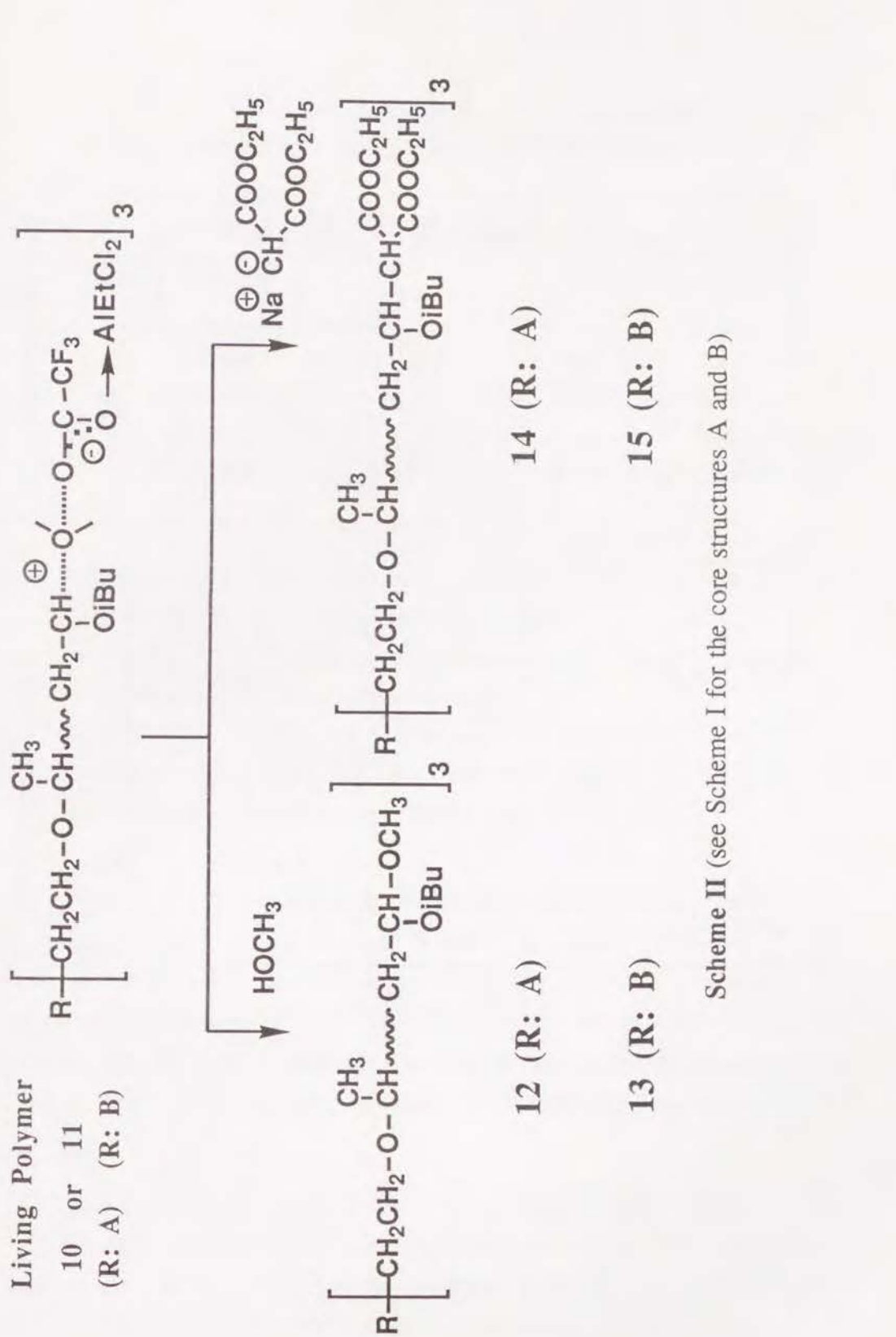
2-3. End-Capping Analysis

In order to confirm the quantitative formation of tri-armed polymers, the living polymers (**10** and **11**) obtained with trifunctional initiator **1** and **2** were terminated with methanol or a solution of sodiomalonic ester (Scheme II), which are known to react, quantitatively and cleanly, with the living end to give methoxy- (**12** and **13**) and malonate-capped poly(IBVE) (**14** and **15**), respectively.[13] For **10** and **11**, the quenching reactions with both quenchers also proceeded rapidly and quantitatively.

Figure 6 illustrates the ^{1}H NMR spectra of the products obtained from living polymer **10** with **1**/$EtAlCl_2$ in *n*-hexane at 0°C. The sample quenched with methanol (Figure 6A) shows all key absortions of the poly(IBVE) main-chain (g – k), the ether-type core A arising from initiator **1** (a – f), and the terminal acetal groups (m and n), all of which confirm the structure expected for polymer **12**. Similarly, Figure 6B for the malonate-capped sample is fully consistent with the structure **14**, as evidenced by the signals for the main-chain (g – k), the ether core A (a – f), and the terminal malonate group (m and n).

The number-average end-functionality ($\overline{F}_n$) of the terminal acetal for **12** or the malonate groups for **14** was determined from the ratios of the integrated ^{1}H NMR peak areas: m/a, m/b, m/c, and m/f (m for the acetal end or for the malonate end; a, b, c, and f are the peaks arising from core A; see Figure 6). As shown in Table I, all $\overline{F}_n$ values, determined from various key peaks independent of each other, are close to three, indicating the existence of three terminals per polymer molecules in both **12** and **14**, or three living ends per molecule for **10**.

Moreover, separate experiments showed the terminal malonic ester of polymer **14** to be quantitatively and cleanly converted into the corresponding carboxyl group [~~~CH_2CH-(OiBu)-CH_2COOH] by the alkaline hydrolysis follwed by thermal decarboxylation to give a tris(carboxy-capped) tri-armed structure.[13a]



Scheme II (see Scheme I for the core structures A and B)

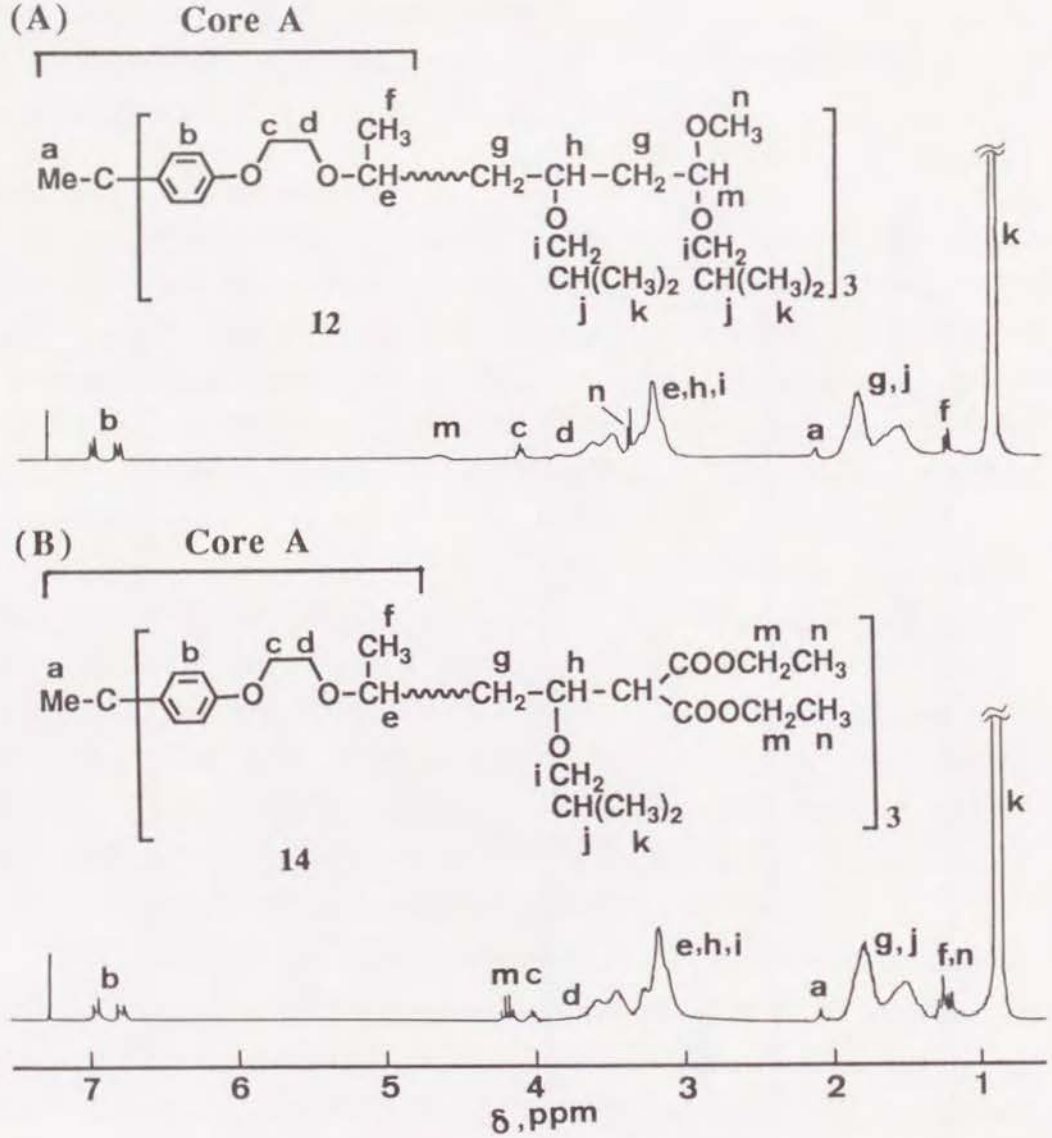


Figure 6. ^{1}H NMR spectra of tri-armed star poly(IBVE): (A) **12**, methoxy-capped; (B) **14**, malonate-capped.

Table I

Synthesis of End-Functional Tri-Armed Star Poly(IBVE)[a]

Code	Structure		$\overline{DP}_n$[b] (calcd)	$\bar{M}_w/\bar{M}_n$[c]	$\overline{DP}_n$[d] (obd)	$\bar{F}_n$[e]			
	Core	Terminal				m/a	m/b	m/c	m/f
12	A	OCH_3	64.5	1.08	62.1	3.03	2.90	2.92	2.90
14	A	$CH(COOEt)_2$	87.3	1.08	84.9	3.09	3.04	2.98	—
13	B	OCH_3	94.9	1.13	92.7	—	3.03	2.98	2.97
15	B	$CH(COOEt)_2$	39.1	1.12	38.1	—	3.01	2.96	—

a) Polymerizations were carried out in *n*-hexane at 0°C; Initiator: **1** for **14**; **2** for **13** and **15**; $[Initiator]_0/[EtAlCl_2]_0$ = 3.5/10 mM.

b) $\overline{DP}_n$(calcd) = ($[IBVE]_0/[2]_0$) x conversion.

c) Measured by size-exclusion chromatography.

d) Determined by ^{1}H NMR, from the peak ratio k/m (see Figures 6 and 7).

e) Number-average end functionality, determined from the ^{1}H NMR intensity ratios of the indicated peaks; see Figures 6 and 7 for spectra.

Very similar results were obtained for the samples that were prepared by quenching the living polymer **11** (with the ester-type core B; Scheme II). The ^{1}H NMR spectra (Figure 7, A and B) of the products again verified the metoxy- (**13**) and the malonate-capped (**15**) terminals as well as the overall tri-armed structure. All $\bar{F}_n$ values are also close to three for both methoxy and malonate terminals (Table I), which shows the trifunctional living ends to present in each molecule of **11**.

2-4. Ester-Core Hydrolysis: Uniformity of Three Arm Chains

Besides the existence of three living ends per molecule, the uniformity in length of three arm chains is another important structural factor that should be verified for well-defined tri-armed polymers. To this end, the ester linkages of

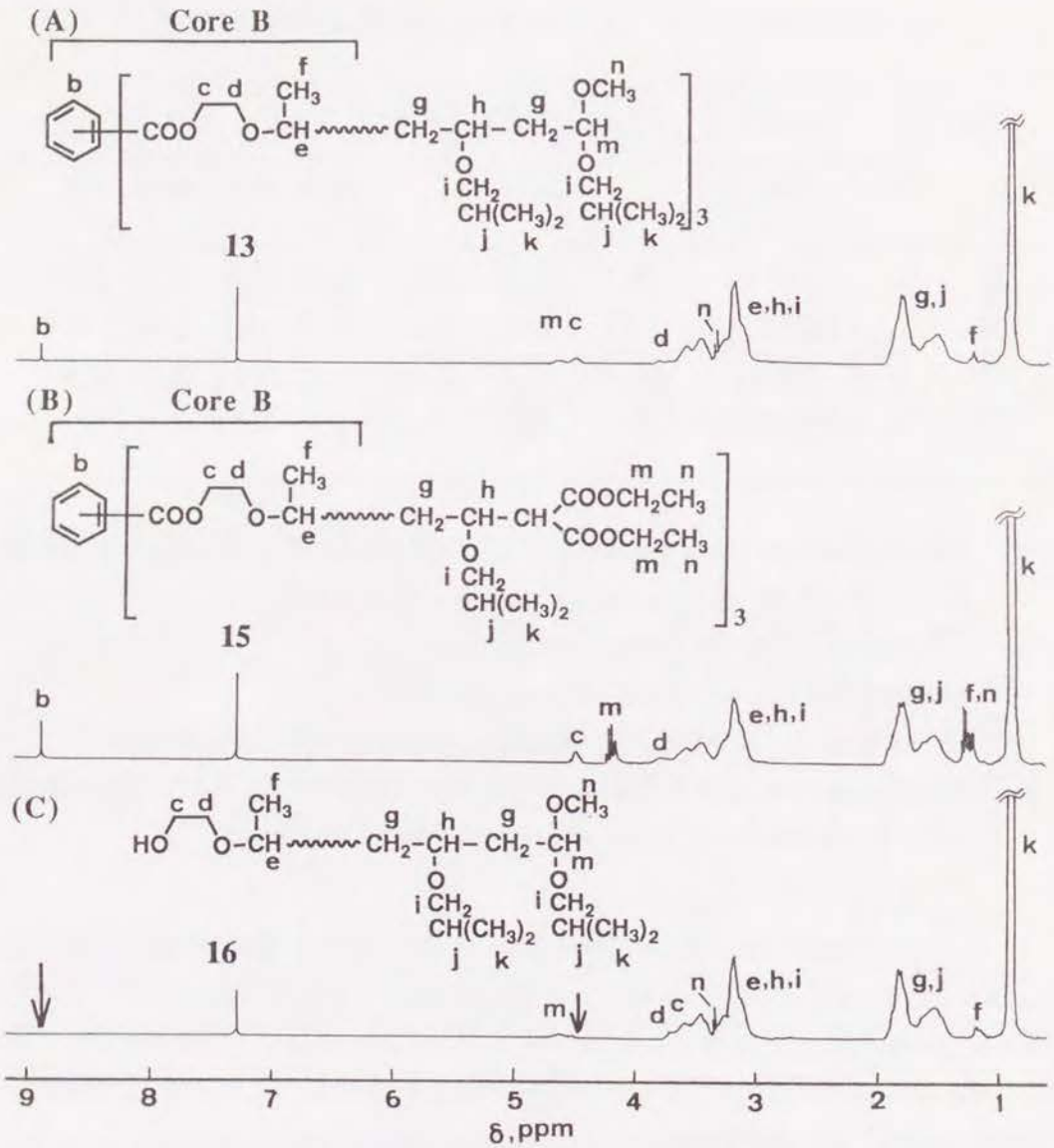
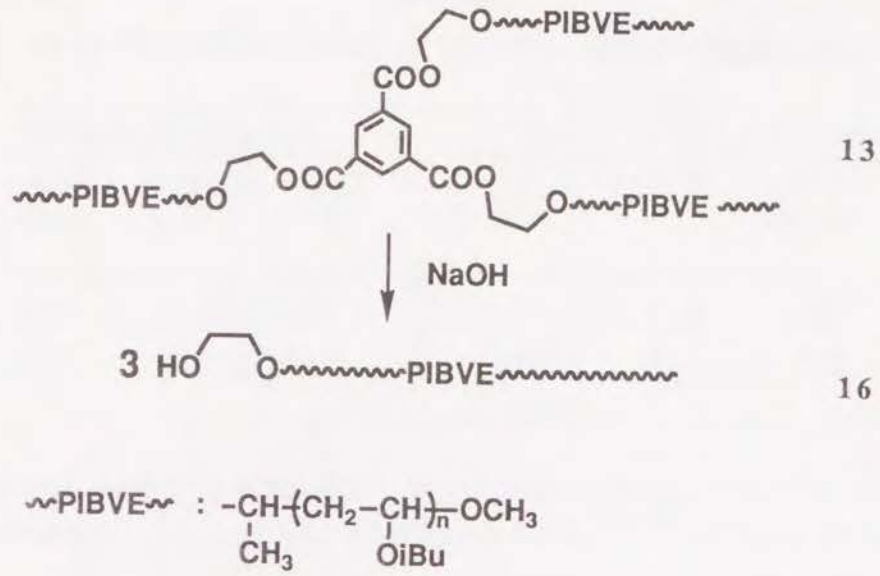


Figure7. ^{1}H NMR spectra of tri-armed star poly(IBVE) (A) **13**, methoxy-capped; (B) **15**, malonate-capped; (C) **16**, the hydrolysis product from **13** (sample A).



13

16

PIBVE : -CH(CH$_3$)-(CH$_2$-CH(OiBu))$_n$-OCH$_3$

Scheme III

polymer **13** (capped with methanol), which connect the three arm chains to the aromatic core, were hydrolyzed under mild alkaline conditions. The core hydrolysis would give three linear arm chains per polymer **13** (Scheme III), from the analysis of which one would see whether or not the starting polymer **11** indeed carries three arms that possess same and uniform chain lengths. Figure 7C shows the ^{1}H NMR spectrum of the hydrolysis product (from the sample of **13** given in Figure 7A). Comparison between spectra 7A and 7C shows the complete conversion of the tri-armed star polymer **13** into a linear arm polymer (**16**) that carries a hydroxyl terminal derived from the ester core. For instance, signals b and c in Figure 7A, due to the core B, are absent in Figure 7C.

The $\overline{DP}_n$ of this sample was determined from the pendant methyl/terminal methine (k/m) ratio, which was nearly one third of the overall $\overline{DP}_n$ of the precursor (**13**); the relevant data are shown in Table II for two series of polymer samples.

Table II

Synthesis and Core Hydrolysis of Tri-Armed Star Poly(IBVE) **13**

Tri-armed Star Poly(IBVE) **13**[a]				Hydrolysis Product **16**[b]		
Conv, %	$\overline{DP}_n$[c] (calcd)	$\bar{M}_w/\bar{M}_n$[d]	$\overline{DP}_n$[e] (obd)	$\overline{DP}_n$ (calcd)	$\bar{M}_w/\bar{M}_n$[d]	$\overline{DP}_n$[e] (obd)
44	94.9	1.13	92.7	31.6	1.14	30.0
100	217	1.12	209	72.4	1.10	71.0

a) Polymerizations were carried out in *n*-hexane at 0°C with **2**/$EtAlCl_2$. $[IBVE]_0$ = 0.76 M; $[\mathbf{2}]_0$ = 3.5 mM; $[EtAlCl_2]_0/[\mathbf{2}]_0$ = 3.0; [1,4-dioxane] = 1.2 M; quenched with methanol.

b) With sodium hydroxide in ethanol at room temperature for 2 days; see Experimental for details.

c) $\overline{DP}_n$(calcd) = $([IBVE]_0/[\mathbf{2}]_0)$ x conversion.

d) From SEC, calibrated with standard polystyrene samples.

e) Determined by ^1H NMR from the peak ratio k/m (see Figure 7, A and C).

Equally important, as shown in Figure 8, the MWD of these polymers (**13** and **16**) remained very narrow even after the core hydrolysis.[12] The peak positions, moreover, clearly shifted, in accordance with the expected molecular weight reduction; see also the relative $\bar{M}_n$ values that are reduced into one third upon hydrolysis, through based on size-exclusion chromatography and a polystyrene calibration.

Table II and Figures 6 and 7, therefore, give direct experimental evidence for the well controlled tri-armed structure of polymer **11** (or **13**), perhaps for the first time for such polymers; namely, **11** possesses exactly three arm chains with a uniform and controlled length ($\overline{DP}_n$) as well as with a very narrow, near monodisperse MWD. Such direct evidence could not be obtained for another

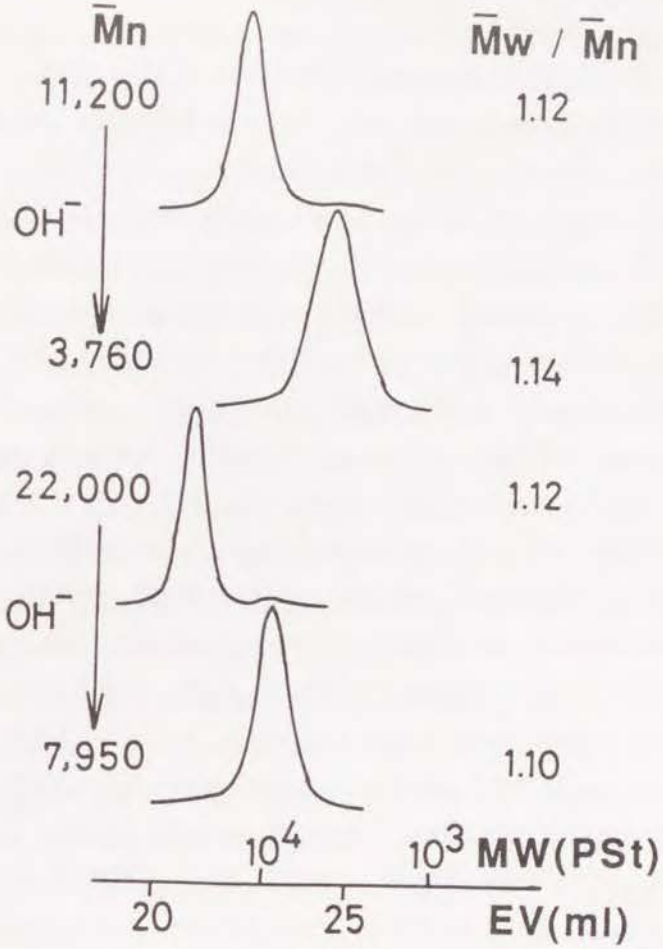


Figure 8 .MWD of tri-armed star poly(IBVE) **13** and its hydrolysis product **16**.

polymer **10**, whose ether type core is chemically stable, but the same conclusion is most likely the case for **10** also, because initiator **1** (for **10**) is less sterically crowded than **2** (for **11**); thus from the former an independent and undisturbed living propagation of the three active sites may be easier than from the latter.

EXPERIMENTAL

Synthesis of Tris(trifluoroacetate) Initiator 1 [Eq (2)]

In a 300 mL, three-necked, round-bottom flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel were charged 1,1,1-tris(4-hydroxyphenyl)ethane (**5**) (Tokyo Kasei, purity 99 %) (10.0 g, 32.6 mmol), powdered NaOH (23.5 g, 0.587 mol), and dimethylsulfoxide (75 mL). After stirred for 30 min at room temperature, the reaction mixture was warmed to 70 – 75 °C in an oil bath, and stirring was continued for an additional 2.5 h. 2-Chloroethyl vinyl ether (59.7 mL, 0.587 mol) was then added slowly via the addition funnel at such a rate as to maintain the temperature below 80°C. When the addition had been completed in 1.5 h, the reaction mixture was kept at 75 – 80°C with stirring for an additional 5 h, cooled to room temperature, and poured into 500 mL of water.

The aqueous phase was extracted with three 50mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed twice with water (100 mL each), dried with sodium sulfate overnight, and evaporated under reduced pressure. The crude product (a yellowich powder) was recrystallized from a toluene/*n*-hexane mixture (1/1 v/v) to give 1,1,1-tris[4-(vinyloxy)ethoxyphenyl]ethane (**6**) as white powder; yield, 62 % from **5**; purtiy > 98 % by ^{1}H NMR (Figure 1A); ^{13}C NMR ($CDCl_3$): δ 156.5 (aromatic carbons adjacent to the oxygen), 151.6 (=CH), 142.0 (aromatic carbons adjacent to the quartenary carbons), 129.5 and 113.7 (unsubstituted aromatic carbons), 86.9 (=CH_2), 66.3 (-CH_2-CH_2-), 50.5 (quartenary carbon), 30.6 (CH_3) ppm.

Trivinyl ether **6** (1.72 g, 3.33 mmol) was then dissolved in 15 mL of CCl_4 at room temperature under dry nitrogen in a baked round-bottom flask equipped with a three-way stopcock, and to this solution was added CF_3COOH (1.14 g, 0.770 mL, 10 mmol) with stirring via a syringe at such a rate as to keep the temperature below 40 °C. The reaction was completed (by 1H NMR) within 15 min after the end of the acid addition. Quantitative formation of **1** was verified in situ by ^{1}H NMR (Figure 1B; see text). The solution was then sealed in brown amples under dry nitrogen and stored in a freezer until employed.

Synthesis of Tris(trifluoroacetate) Initiator 2 [Eq (3)]

In a 200 mL, three-necked, round-bottom flask fitted with a stirrer, a reflux condenser, and a dropping funnel were charged 2-hydroxyethyl vinyl ether (Nisso Maruzen Chemical, purity > 99 %, H_2O < 1 %) (9.96 g, 0.113 mol), sodium hydride (2.71 g, 0.113 mol) and toluene (50 mL); the sodium hydride (supplied commercially as an oil dispersion) was made free from mineral oil by washing with toluene just before use. The mixture was stirred at room temperature for 1 h, and trimessic chloride **7** (Aldrich, purity 98 %) (10.0 g, 33.7 mmol, dissolved in 20 mL DMF) was added dropwise through the dropping funnel. After the addition had been completed, tetra-*n*-butylammonium iodide (0.5 g) was added. The mixture was then warmed to +80°C in 30 min in an oil bath, stirred at this temperature for 4 h, cooled to room temperature, and poured into 200 mL of water. The aqueous phase was extracted with three 50 mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed twice with water (100 mL each), dried with sodium sulfate overnight, and evapolated under reduced pressure. The crude product (a yellowish powder) was recrystallized twice from a toluene/*n*-hexane mixture (1/1 v/v) to give tri(2-vinyloxy)ethyl 1,3,5-benzenetricarboxylate **8** as a white powder; yield, 74 % from **7**; purity > 98 % by ^{1}H NMR (Figure 2A); ^{13}C NMR ($CDCl_3$): δ 164.7 (C=O), 151.4 (=CH), 134.9 and 131.0 (aromatic carbons), 87.2 (=CH_2), 65.5 and 63.8 (-CH_2CH_2-) ppm.

In a manner similar to those for **1**, tris(trifluoroacet-ate) initiator **2** was prepared from trivinyl ether **8** and CF_3COOH (see also Figure 2B).

Monofunctional Initiators 3 and 4

In a manner similar to those for **1** and **2**, initiators **3** and **4** were prepared from 2-(phenoxy)ethyl and 2-(benzoyloxy)ethyl vinyl ethers, respectively, both of which were obtained by the reported methods.[14,15] ^{1}H NMR ($CDCl_3$): **3**, δ 7.10 and 6.70 (5H, aromatic protons), 6.00 (q, 1H, CH), 3.90 (m, 4H, -CH_2CH_2-), 1.40 (d, 3H, CH_3); **4**, δ 8.05, 7.55 and 7.40 (5H, aromatic protons), 6.10 (q, H, CH), 4.45 and 4.00 (m, 4H, -CH_2CH_2-), 1.55 (d, 3H, CH_3) ppm.

Other Materials

Commercial IBVE was washed with an aqueous alkali solution and then water, dried (KOH pellets), and distilled twice over calcium hydride before use. Commercial $EtAlCl_2$ (Kanto Chemicals, 1.0 M *n*-hexane solution) and CF_3COOH (Nakarai Chemicals, purity > 99 %, supplied in sealed ampules) were used under dry nitrogen without futher purification. *n*-Hexane (polymerization solvent), 1,4-dioxane (added base), and *n*-heptane (internal standard for gas chromatography) were purilied by the usual methods[16] and distilled twice over calcium hydride just before use. Sodiomalonic ester (100 mM solution in 1,4-dioxane) was prepared as reported.[13a]

Procedures

IBVE was polymerized with the **1** (or **2**)/$EtAlCl_2$ initiating system at 0 °C in the presence of 1,4-dioxane (10 vol%) under dry nitrogen in baked glass tubes each equipped with a three-way stopcock. The reactions were initiated by adding, sequentially, prechilled solutions of initiator **1** (or **2**) and $EtAlCl_2$ (in toluene and *n*-hexane, respectively; 0.50 mL each) to a monomer solution (in *n*-hexane; 4.0 mL). After a predetermined period, the polymerization was terminated with prechilled methanol containing ammonia or with the solution of sodiomalonic ester [2.5 mL; 10 equiv to **1** or **2** (living end)]. The quenched reaction mixtures were washed sequentially with 10 vol % aqueous hydrochloric acid and then with water to remove the aluminum-containing residues, evaporated to dryness under reduced pressure, and vacuum dried overnight to give the product polymers. IBVE conversion was measured by gravimetry of the product polymers or for some runs by gas chromatography with *n*-heptane as an internal standard (2.5 or 5.0 vol%).

Core Hydorolysis of 13

A sample of tri-armed star poly(IBVE) **13** (0.1 g) was dissolved in ethanol (10 mL), and 5N sodium hydroxide (50 equiv to the ester units in the polymer) was added. The mixture was magnetically stirred for 3h, water (10 mL) was added, and stirring was continued for an additional two days. The product **16**, was extracted with diethyl ether, washed with water, and then isolated by evapolation followed by vacuum-drying.

Polymer Characterization

The MWD of the products was determined by size-exclusion chromatography in chroloform at room temperature on a Jasco Trirotar chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and K-804; 8.0 mm i.d. × 300 mm each) and refractive index/ultraviolet dual detectors. The number-avarage molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from size-exclusion eluograms on the basis of a polystyrene calibration. ^1H and ^{13}C NMR spectra (270 and 67.5 MHz, respectively) were recorded at +22°C on a Jeol GSX-270 spectrometer in $CDCl_3$.

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12. The small peaks seen in the low molecular weight region in Figure 5B and 8 for the tri-armed polymers are probably due to monofunctional (living) polymers that might have been initiated by a protonic source (most likely a trace of free CF_3COOH coming from the preparation of **1** or **2**). The reasons are as follows: (a) the absence of UV absorption; thus this fraction is not derived from an incomplete initiation from the trifunctional initiator; (b) its formation from the beginning of the polymerization; thus it is not due to chain transfer or termination; (c) the molecular weight ($\bar{M}_n$) that is one third that of the trifunctional polymer and directly proportional to conversion.
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CHAPTER 6

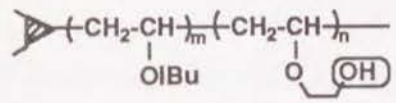
TRI-ARMED AMPHIPHILIC STAR BLOCK COPOLYMERS OF ISOBUTYL AND 2-HYDROXYETHYL VINYL ETHERS

ABSTRACT

Tri-armed amphiphilic block polymers (**5** and **6**) of isobutyl and 2-hydroxyethyl vinyl ethers (IBVE and HOVE, respectively) were prepared. The synthesis was based on the sequential living cationic polymerization of IBVE and 2-acetoxyethyl vinyl ether (AcOVE) initiated with a trifunctional initiating system that consisted of a tris(trifluoroacetate)

CH_3-C-[C_6H_4-OCH_2CH_2O-$CH(CH_3)OCOCF_3$ (*p*-)]$_3$ (**1**)

and ethylaluminum dichloride ($EtAlCl_2$) coupled with an excess of 1,4-dioxane as a carbocation-stabilizing Lewis base. The subsequent hydrolysis of the ester pendant groups in the resulting poly(AcOVE) segments led to the target IBVE-HOVE amphiphilic tri-armed polymers. Depending on the polymerization sequence of IBVE and AcOVE, the hydrophilic poly(HOVE) chain could be placed either inner or outer segment of the tri-armed architecture. The solubility of these polymers (**5** and **6**) was apparently determined by the nature of the outer segments.



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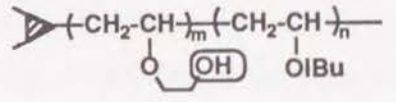

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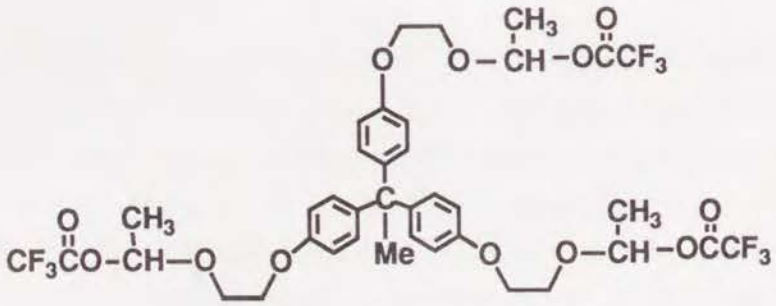
: CH_3-C-[C_6H_4-OCH_2CH_2O-$CH(CH_3)$- (*p*-)]$_3$

INTRODUCTION

In the preceding Chapter,[1] the author has discussed the development of a trifunctional initiating system, consisting of a tris(trifluoroacetate) (**1**) and ethylaluminum dichloride ($EtAlCl_2$), that induces living cationic polymerization of isobutyl vinyl ether (IBVE) in the presence of 1,4-dioxane at relatively high temperatures up to +40°C. The initiator **1** is derived from the corresponding trifunctional vinyl ether and, with aid of $EtAlCl_2$, each of the three vinyl ether-derived trifluoroacetate groups of **1** initiates polymerization of IBVE to generate a trifunctional living polymer **2** [Eq (1)] where the active cationic site is stabilized by the added 1,4-dioxane as a mild base. The product is a tri-armed poly(IBVE) that is featured by the uniformity in length of three arm chains, in addition to a controlled overall molecular weight and a very narrow molecular weight distribution (MWD).



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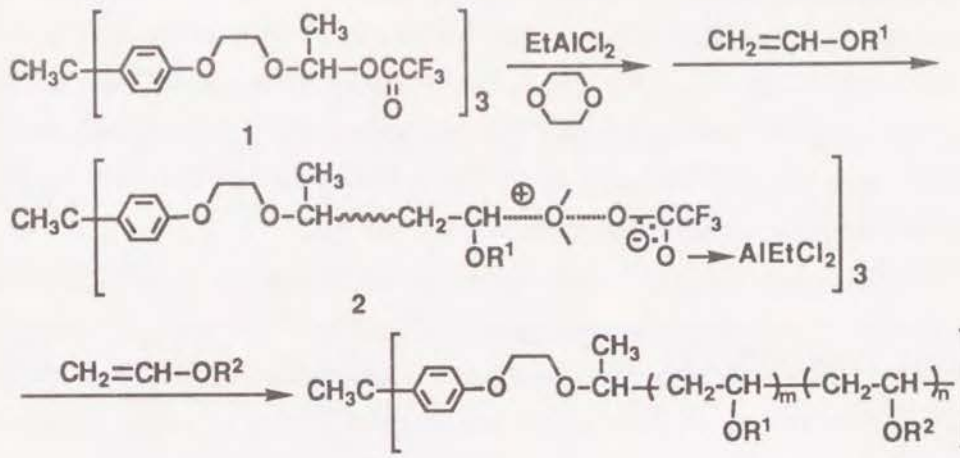
This chapter deals with the application of the **1**/$EtAlCl_2$/1,4-dioxane system to sequential living cationic polymerization of IBVE and an ester-functionalized vinyl ether [2-acetoxyethyl vinyl ether (AcOVE)] [Eq (1)], which was directed to the synthesis of novel tri-armed amphihpilic block copolymers of IBVE (hydrophobic) and 2-hydroxyethyl vinyl ether (hydrophilic), the latter being derived from hydrolysis of the AcOVE segment. Such tri-armed block polymers with polar functional groups have not been obtained in cationic polymerization yet.



Code	R^1 (Inner)	R^2 (Outer)
3	$CH_2CH(CH_3)_2$	$CH_2CH_2OCOCH_3$
4	$CH_2CH_2OCOCH_3$	$CH_2CH(CH_3)_2$

RESULTS AND DISCUSSION

1. Block Polymerization

With use of the **1**/$EtAlCl_2$ trifunctional initiating system, sequential living polymerization of IBVE and AcOVE was examined [Eq (1)], starting either with IBVE (for **3**) or with AcOVE (for **4**). For example, in the presence of 1,4-dioxane, IBVE was first polymerized in toluene at 0°C with **1**/$EtAlCl_2$.[1] The polymerization reached quantitative monomer conversion in 6 min. To the solution of the resulting tri-armed living polymer (**2**), AcOVE was added, and the temperature was raised to +40°C to accelerate the polymerization of AcOVE, which is less reactive than IBVE. The added AcOVE feed was polymerized completely in 3 h.

The reverse order of monomer addition, i.e., from AcOVE to IBVE, was also examined. Thus, AcOVE was first polymerized with **1**/$EtAlCl_2$ in the presence of 1,4-dioxane at +40°C. The polymerization was completed after 2 h, at which moment IBVE was added, and it was quantitatively polymerized in an additional 1 h at the same temperature. Figure 1 shows the MWD curves for the products of these two series of sequential polymerizations.

The first-stage polymerizations led to polymers of narrow MWDs ($\bar{M}_w/\bar{M}_n$ < 1.1), not only from IBVE as already reported (Figure 1A)[1] but also from AcOVE (Figure 1C). The MWDs obtained after the second monomer addition (Figures 1B and 1D) were as narrow as those of the first-stage polymers and clearly shifted toward higher molecular weight without tailings in the regions where the starting polymers eluted. The MWD analysis thus suggests the formation of living polymers in all these sequential polymerizations.

The structure and segment compositions of these block polymerization products were determined by ^1H NMR spectroscopy (Figures 2 and 3). These samples are the same for those shown in Figure 1, and they were quenched with methanol, which is known to give a methoxide (acetal) terminal [~~$CH_2CH(OR)$-OCH_3].[1] For example, Figure 2 presents typical ^1H NMR spectra of the starting poly(IBVE) (Figure 2A) and the product after the addition of AcOVE (Figure 2B).

Figure 2A is completely consistent with the tri-armed poly(IBVE) derived from the initiator **1**, showing, for instance, the absorptions of the pendant methyl groups (peak d) and the aromatic initiator residue (peak a). In addition to these, the absoption of the acetoxy groups arising from AcOVE (peaks f and g) are seen in Figure 2B, confirming the structure expected for the tri-armed star block poly(IBVE-*b*-AcOVE) **3**.

Very similar results were obtained for the samples prepared through the opposite polymerization sequence (AcOVE-IBVE) (Figures 3A and 3B) and corroborated the formation of a tri-armed poly(AcOVE-*b*-IBVE) [**4**, Eq (1)].

The starting homopolymer of AcOVE (Figure 3A), for example, exhibited a spectrum indicative of the tri-armed structure, as evidenced by peaks f and g for the pendant acetoxyethyl groups and peak a for the initiator aromatic protons. The

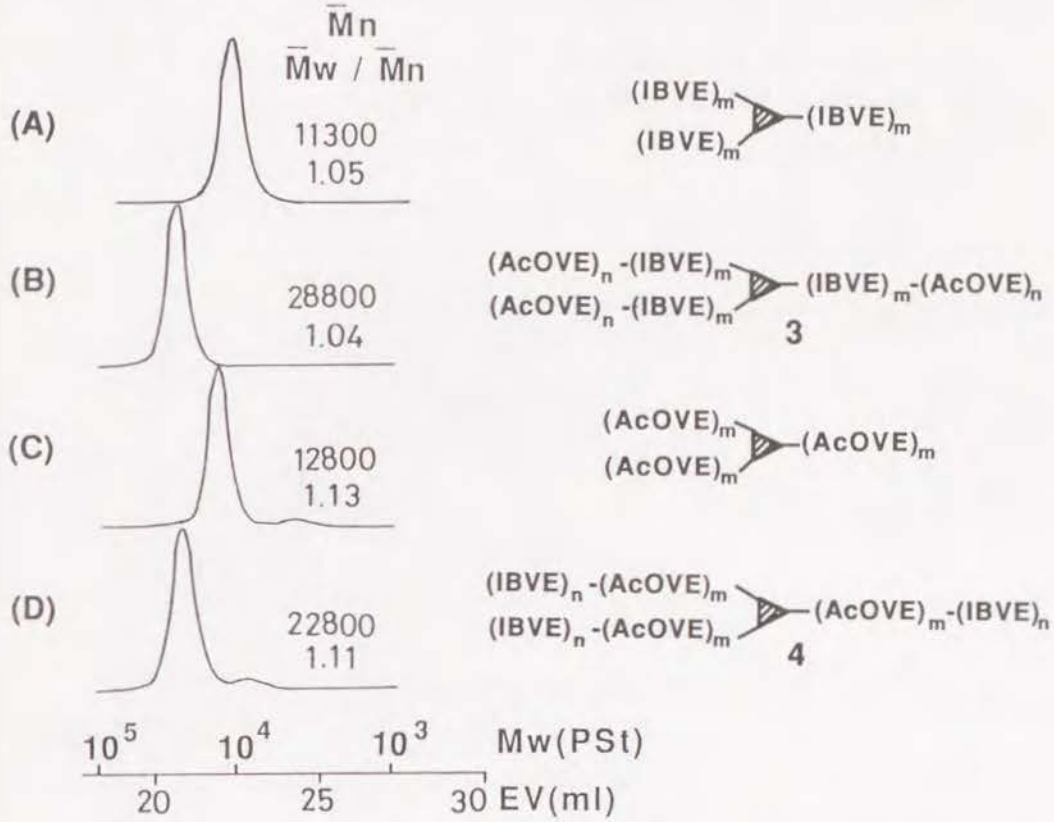


Figure 1. MWD of tri-armed homopolymers and block polymers of IBVE and AcOVE obtained by sequential living polymerization with trifunctional initiator (**1**)/$EtAlCl_2$ at +40°C in toluene containing 1,4-dioxane: $[IBVE]_0 = [AcOVE]_0 = 0.38$ M; $[\mathbf{1}]_0 = 3.5$ mM; $[EtAlCl_2]_0 = 10.0$ mM; [1,4-dioxane] = 1.2 M (10 vol%); conversion = 100 % for all monomers. Samples and reaction times: (A) starting poly(IBVE), 6 min (at 0°C); (B) poly(IBVE-*b*-AcOVE) **3** from sample A, 3 h after AcOVE addition; (C) starting poly(AcOVE), 2 h; (D) poly(AcOVE-*b*-IBVE) **4** from sample C, 1 h after IBVE addition. ▶ shows the aromatic core derived from initiator **1** [see Eq (1)].

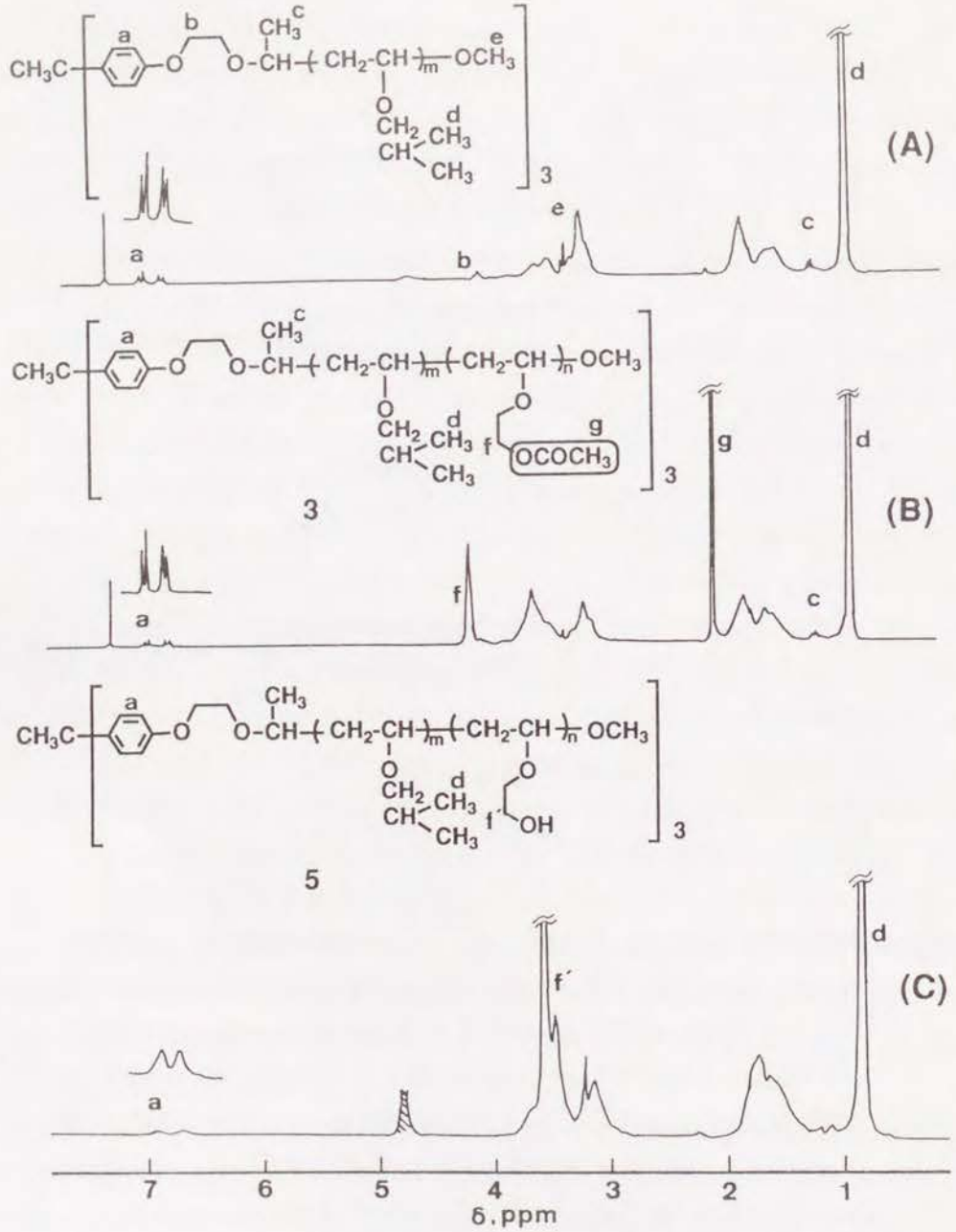


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Figure 2. ^{1}H NMR spectra in $CDCl_3$ (A and B) or CD_3OD (C):

(A) tri-armed poly(IBVE);

(B) tri-armed poly(IBVE-*b*-AcOVE) **3** from sample A;

(C) tri-armed poly(IBVE-*b*-HOVE) **5** from sample B after hydrolysis.

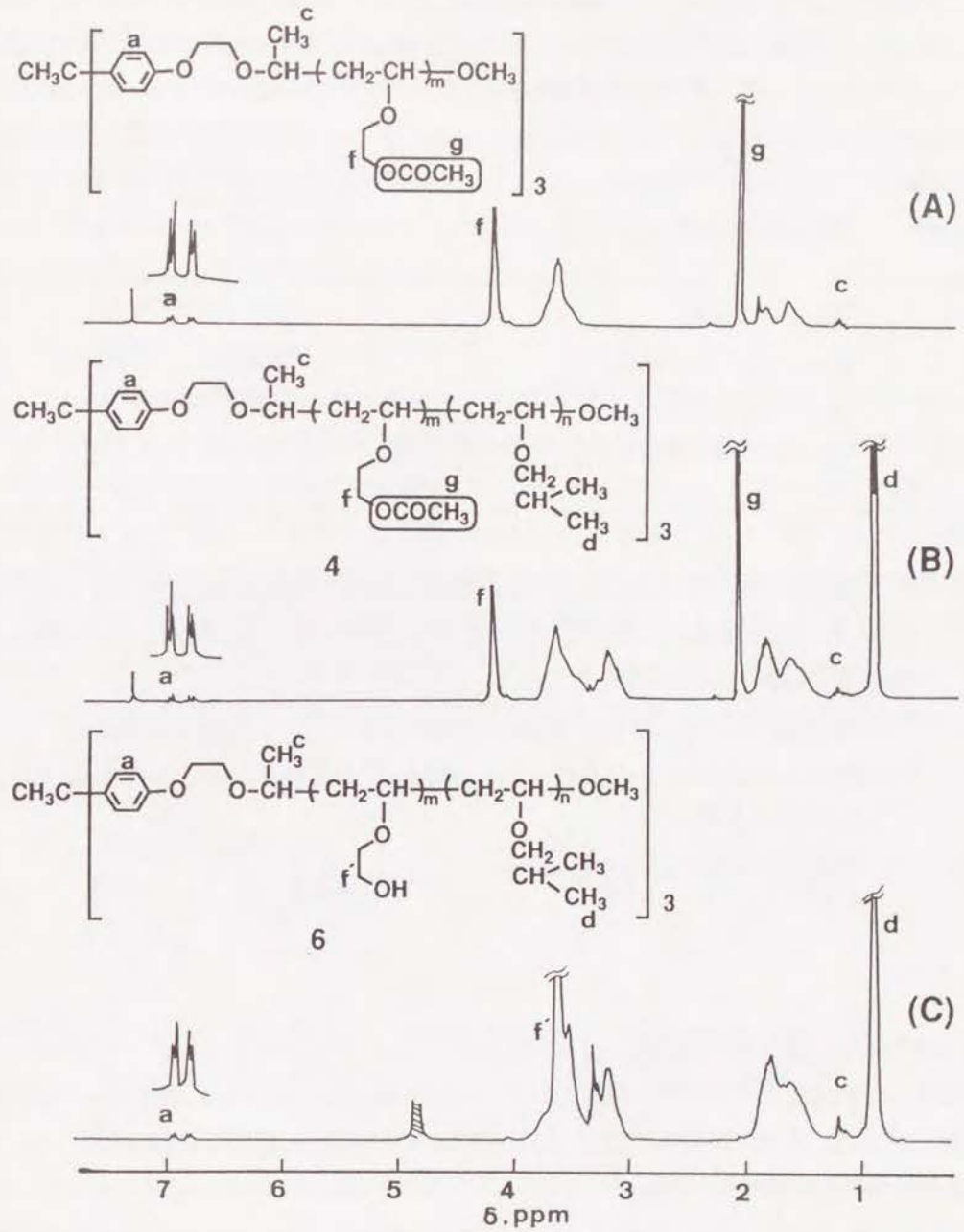

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Figure 3. ^{1}H NMR spectra in $CDCl_3$ (A and B) or CD_3OD (C):

(A) tri-armed poly(AcOVE);

(B) tri-armed poly(AcOVE-*b*-IBVE) **4** from sample A;

(C) tri-armed poly(HOVE-*b*-IBVE) **6** from sample B after hydrolysis.

Table I

Tri-Armed Star Block Copolymers of IBVE and AcOVE via Sequential Living Cationic Polymerization with **1**/$EtAlCl_2$[a]

Code	Tri-armed Polymer ▷—(-A-b-B-)- [b]	Segment $\overline{DP}_n$, A/B[b,c] calcd[d]	obsd[e]
	▷—**IBVE**	38	36
3	▷—**IBVE-AcOVE**	38/38	36/38
	▷—**AcOVE**	38	35
4	▷—**AcOVE-IBVE**	38/38	35/34

b) A indicates the monomer that was first polymerized into a living polymer from which the second monomer B is polymerized; ▷ shows the aromatic core derived from initiator **1** [see Eq (1)].

c) The number-average degree of polymerization ($\overline{DP}_n$) for each segment.

d) Calculated from the initial concentrations of the monomers and **1**: segment $\overline{DP}_n(calcd) = [M]_0/[\mathbf{1}]_0$.

e) By ^1H NMR spectroscopy; see text.

second-stage polymerization of IBVE led to the spectrum shown in Figure 3B, which is almost identical to Figure 2B and shows the resonances of poly(IBVE) segment (e.g., peak d) in addition to those for the poly(AcOVE) segments.

To demonstrate the formation of true AB-type tri-armed block copolymers (**3** and **4**), the number-avarage degree of polymerization ($\overline{DP}_n$) of each segment was determined by ^1H NMR from the peak intensity ratio of the aromatic initiator residue (peak a; both Figures 2 and 3) to the pendant resonance of the poly(IBVE) or poly(AcOVE) segments; the key pendant signals: the methyl protons of the isobutyl group (peak d; 0.9 ppm) for IBVE and the methylene protons associated

with the acetate group (peak f; 4.2 ppm) for AcOVE. As Table I summarizes, the observed $\overline{DP}_n$ values were in good agreement with the calculated values based on the feed molar ratios of IBVE or AcOVE to the initiator **1**. The spectral analysis thus confirmed the formation of the desired tri-armed AB block copolymers of IBVE and AcOVE in nearly perfect blocking efficiency. It should also be important that living cationic polymerization with **1**/$EtAlCl_2$ (+ 1,4-dioxane) is now feasible for AcOVE, an ester functionalized polar vinyl ether.

2. Amphiphilic Block Copolymers

The acetate groups of the tri-armed IBVE-AcOVE block copolymers **3** and **4** were then hydrolyzed to give amphiphilic tri-armed star block polymers **5** and **6**, respectively, carrying polyalcohol [poly(HOVE)] segments derived from AcOVE. Note that polymers **5** and **6** are the same in segment $\overline{DP}_n$ and composition (IBVE/HOVE = 38/38 in $\overline{DP}_n$) but are opposite in segment arrangement; the polyalcohol hydrophilic segments are located outside the molecules in **5**, whereas inside in **6** (see schematic illustrations below where ▬ and ∿∿ show the hydrophilic poly(HOVE) and the hydrophobic poly(IBVE) segments, respectively):

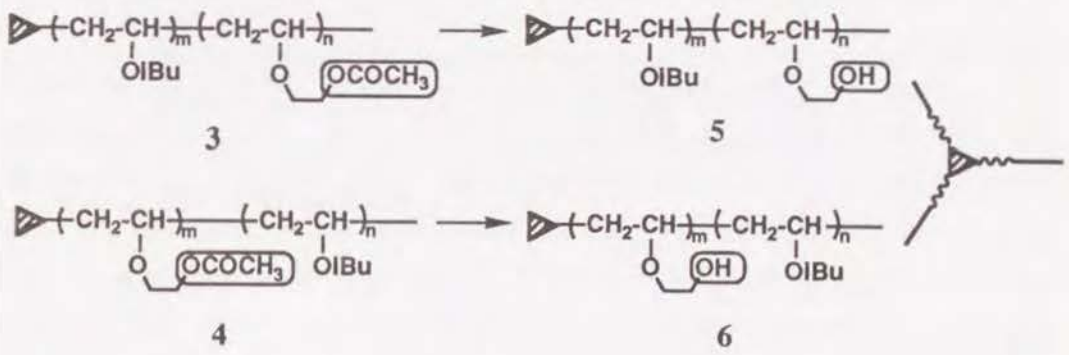

Figure 2C illustrates the ^1H NMR spectrum (in CD_3OD) of the hydrolysis product obtained from **3** [with outer poly(AcOVE) chains; Figure 2B]. Comparison between spectra 2B and 2C shows the complete conversion of the pendant acetoxy groups into the corresponding alcohol. For example, signals f and g in Figure 2B, associated with the acetoxy group, are absent in Figure 2C, where

the methylene protons due to the alcohol group are in turn seen around 3.6 ppm (peak f'). The spectral analysis thus shows the formation of the new amphiphilic tri-armed block copolymer (**5**) with outer polyalcohol segments. In a similar manner, as Figure 3C illustrates, the hydrolysis of **4** led to another tri-armed amphiphile **6** with inner polyalcohol segments. Interestingly, the aromatic protons' signals of the initiator core (peak a; 6.6-7.0 ppm) were clearly broader for **5** (with outer polyalcohol; Figure 2C) than for **6** (with inner polyalcohol; Figure 3C), probably because the hydrophobic inner poly(IBVE) segments in **5**, to which the aromatic core is attached, shrink in relatively polar CD_3OD solvent and thereby restrict the thermal movement of the core.

3. Solubility Characteristics

Table II summarizes the solubility characteristics of the tri-armed block polymers obtained in this study. First, the four AcOVE-based polymers B-E are all soluble in toluene but insoluble in water, whereas their hydrolysis products (HOVE-based polymers, F-I) are more polar and, as expected, now insoluble in toluene

and *n*-hexane but soluble or swellable in water. These trends are fully consistent with the transformation of the poly(AcOVE) segments into more polar poly(HOVE) counterparts.

As seen in the first group (B-D), moreover, the overall solubility characteristics of the tri-armed block polymers (C and D) appear to be governed primarily by the nature of the outer segments. Thus, sample C is the same in solubility as homopoly(AcOVE) (B), and sample D as homopoly(IBVE) (A). The corresponding linear analog (E), however, has intermediate solubility properties between C and D. It is equally interesting that even moving the modelately polar AcOVE segment from the inner (D) to the outer (C) region of the tri-armed architecture renders sample C insoluble in *n*-hexane and ethanol, which are good solvents for sample D.

In contrast, the HOVE-based polymers (F-I) are more or less similar in solubility, regardless of the placement of the polar polyalcohol segments (G vs. H)

Table II

Solubility of Tri-Armed Star Poly(vinyl Ethers)[a,b]

Entry	Polymer		Solvent				
	Shape	Inner/Outer	toluene	hexane	EtOH	MeOH	H_2O
A	Tri-armed	**IBVE**	O	O	O	X	X
B	"	**AcOVE**	O	X	X	O	X
C	"	**IBVE/AcOVE (3)**	O	X	X	O	X
D	"	**AcOVE/IBVE (4)**	O	O	O	X	X
E	Linear	**AcOVE/IBVE**	O	O	O	O	X
F	Tri-armed	**HOVE**	X	X	O	O	O
G	"	**IBVE/HOVE (5)**	X	X	O	O	O
H	"	**HOVE/IBVE (6)**	X	X	Δ	O	Δ
I	Linear	**HOVE/IBVE**	X	X	Δ	O	Δ

a) **O**, soluble; Δ, swelling; **X**, insoluble. At room temperature ca. 0.5 wt%. $\overline{M}_w/\overline{M}_n < 1.1$ for all samples.

b) The calculated values for respective segments. $\overline{DP}_n$ is invariably 38 for each arm segment; e.g., sample A consists of three homopoly(IBVE) arms each with 38 IBVE units; sample C carries three AB block arms, each with 38 IBVE and 38 AcOVE units.

or even of the presence and absence of the nonpolar poly(IBVE) part (F vs. G and H). However, the poly(HOVE) segment in the outer region (G) indeed increased the solubility in water and ethanol, where the inner-alcohol version (H) just swells but remains not totally soluble.

EXPERIMENTAL

The syntheses of initiator **1**[1] and AcOVE[2] have already been described. IBVE, toluene, 1,4-dioxane, and $EtAlCl_2$ were employed as reported.[1,3] Block polymerizations of IBVE and AcOVE were carried out under dry nitrogen by sequential addition of solutions of **1** (in toluene; 0.50 mL) and $EtAlCl_2$ (in *n*-hexane; 0.50 mL) into a mixture of the first monomer and 1,4-dioxane (0.50 mL; 1.2 M; 10 vol%) in toluene (3.50 mL).[1] Immediately before the end of the first-stage polymerization, the second monomer in bulk was added to the reaction mixture; see the caption for Figure 1 for reaction times, reagent concentrations, etc. After the complete consumption of the second monomer, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. The alkaline hydrolysis of the block polymers was carried out as reported.[2,4]

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CHAPTER 7

TRI-ARMED STAR POLYMERS OF *p*-METHOXYSTYRENE

ABSTRACT

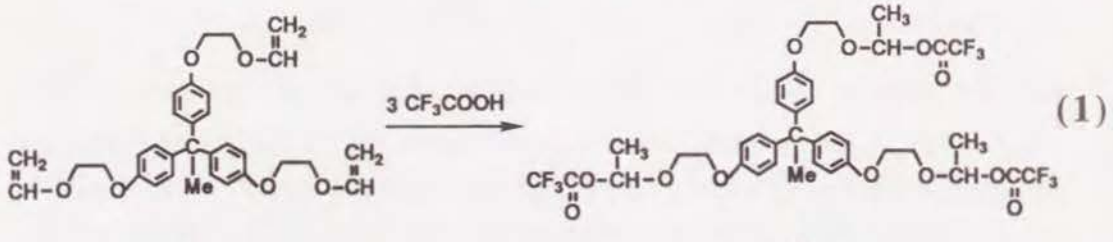
Tri-armed star polymers of *p*-methoxystyrene (pMOS) were synthesized by living cationic polymerization by a trifunctional initiator (**6** or **9**):

CH_3-C-[$C_6H_4OCH_2CH_2OCH(CH_3)$-I (*p*-)]$_3$ (**6**)
C_6H_3-[$COOCH_2CH_2OCH(CH_3)$-I]$_3$ (1,3,5-) (**9**)

with zinc iodide as activator in toluene at -15°C. The number-average molecular weight ($\bar{M}_n$) of the polymers thus prepared increased in direct proportion to monomer conversion and further increased upon addition of fresh feeds of pMOS into completely polymerized reaction mixtures; the polymers invariably exhibited very narrow molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n < 1.1$). The living polymers were terminated with 2-hydroxyethyl methacrylate to give a tri-armed macromonomer where each arm is capped with a methacrylate group, and the quantitative end-capping, in turn, showed the existence of three living ends per molecule. When the ester-type initiator residue (core) of the poly(pMOS), obtained with the **9**/ZnI_2 system, was hydrolyzed under alkaline conditions, the $\bar{M}_n$ was reduced to one third of the original value, with the narrow MWD unchanged, thus indicating that the polymer possesses three arm chains with a uniform and controlled length.

INTRODUCTION

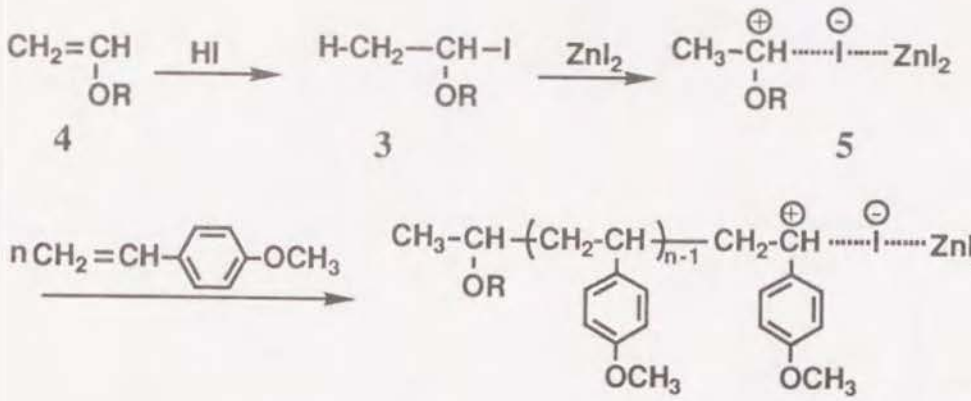
As described in Chapter 5,[1] the auther has developed a trifunctional initiator (**1**) that is prepared by addition of 3 equivalents of trifluoroacetic acid to a trifunctional vinyl ether (**2**) [Eq (1)]. Coupled with ethylaluminum dichloride (as Lewis acid activator) in the presence of 1,4-dioxane (as stabilizer of carbocation), initiator **1** induces living cationic polymerization of vinyl ethers to form tri-armed star poly(vinyl ethers)[1,2] that possess exactly three arm chains per molecule with a uniform and controlled length. Though highly efficient, the applicability of this tris(acetate)-type initiator **1** has been confined to vinyl ethers.



2 **1** (1)

The auther has also found that living cationic polymerizations of *p*-methoxy- and *p*-*t*-butoxystyrenes can be initiated not only with the classical HI/ZnI_2 system[3,4] but also with a cationogen (**3**) derived from a vinyl ether (**4**) and hydrogen iodide in the presence of zinc iodide (ZnI_2) activator [Eq (2)].[5] The living polymerizations by the **3**/ZnI_2 systems follow the nearly identical pathways with those originally initiated by the HI/ZnI_2 counterpart, and it is important that the vinyl-ether type carbocation **5** can polymerize *p*-alkoxystyrenes, which are less reactive than vinyl ethers.

Based on this initiation process via the hydrogen iodide-based initiators, the study to be described in the present chapter concern development of a trifunctional initiator for living cationic polymerization of pMOS and the synthesis of tri-armed polymers of pMOS including those with terminal functional groups.



(2)

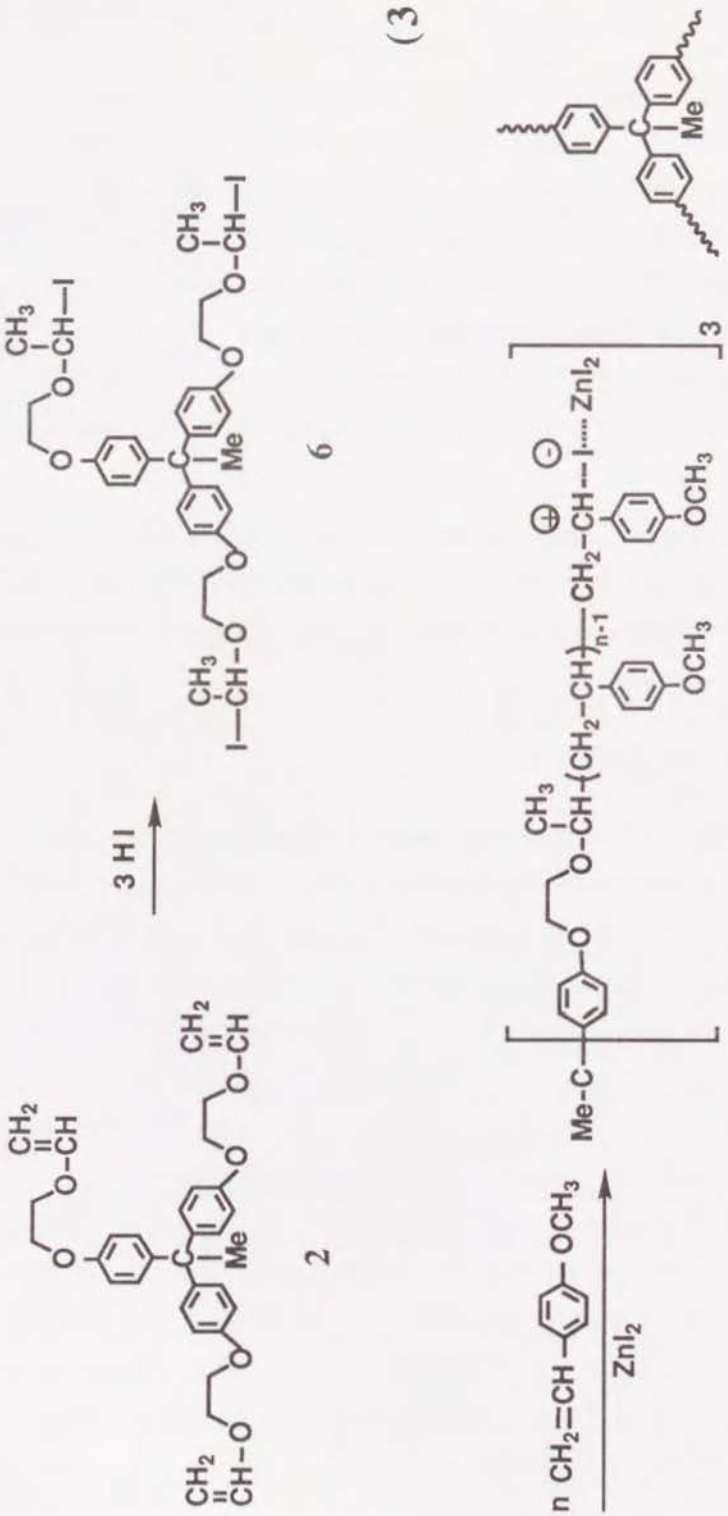
As shown in Eq (3), a trifunctional initiator **6** was prepared by the treatment of a trifunctional vinyl ether **2** with 3 equivalents of hydrogen iodide. pMOS was polymerized at -15°C by **6** coupled with ZnI_2 to give tri-armed living poly(pMOS) **7**.

RESULTS AND DISCUSSION

1. Living Cationic Polymerization with Trifunctional Initiator

According to the route illustrated in Eq (3), trifunctional initiator **6** was prepared by the reaction of trifunctional vinyl ether **2**[1] with 3 equivalents of hydrogen iodide at -78°C in a toluene/*n*-hexane mixed solvent (1/1 v/v).[5] The as-prepared solution of **6** was then employed to polymerize pMOS in the presence of ZnI_2 in toluene at -15°C, typically under the following conditions: $[pMOS]_0 = 0.38$ M, $[\mathbf{6}]_0 = [ZnI_2]_0 = 3.3$ mM. A smooth polymerization occurred without an induction phase to reach quantitative conversion within 90 min.

Figure 1A illustrates the MWDs of the polymers thus obtained. All polymers possessed narrow MWDs that progressively shifted towards higher molecular weight as the reaction proceeded. In each MWD curve, however, there is seen a small peak at a molecular weight about one third that of the main peak; the minor fraction is most likely due to the initiation by free hydrogen iodide that might be slightly in excess over vinyl ether **1**.



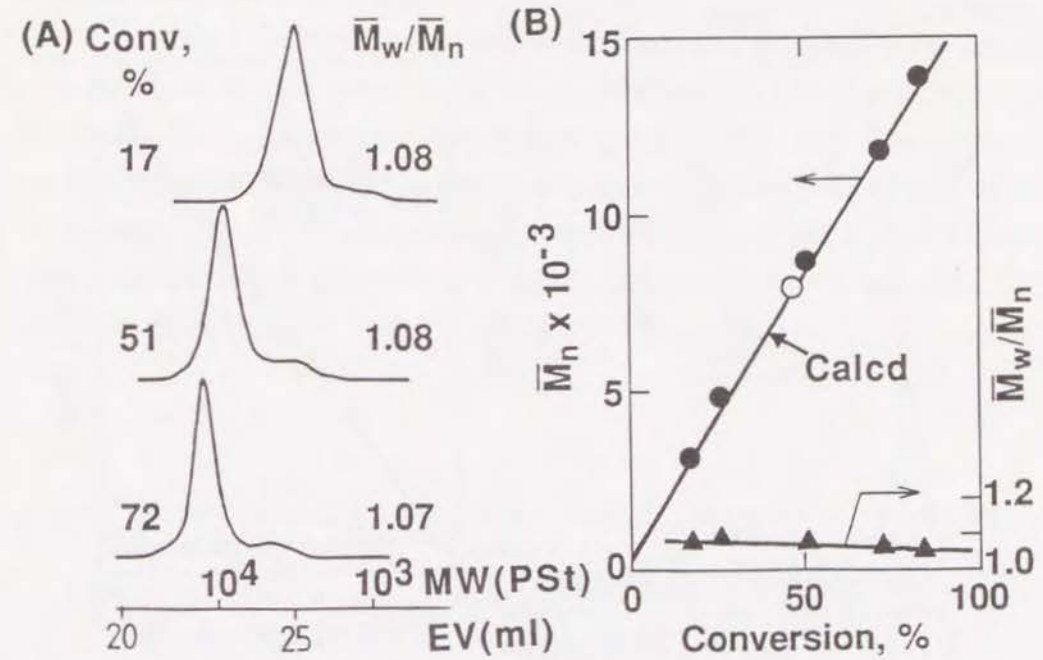


Figure 1. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of tri-armed star poly(pMOS) obtained with trifunctional initiator (**6**)/ZnI_2 in toluene at -15°C. $[pMOS]_0 = 0.38$ M; $[\mathbf{6}]_0 = 3.3$ mM; $[ZnI_2]_0 = 3.3$ mM. (●,▲) by size-exclusion chromatography with a polystyrene calibration; (**O**) by ^1H NMR (cf. Figure 3)

The MWDs of the main peaks were very narrow ($\bar{M}_w/\bar{M}_n < 1.1$), and the $\bar{M}_n$ values, based on a polystyrene calibration, increased in direct proportion to monomer conversion and were approximately in agreement with the calculated values based on the assumption that one polymer chain forms per initiator (Figure 1B). The quantitative initiation from **6** was further confirmed by determining the absolute molecular weights of the polymers by ^1H NMR, as discussed later in this chapter. These facts show that living polymerization of pMOS is initiated by the trifunctional initiator **6** in conjunction with ZnI_2.

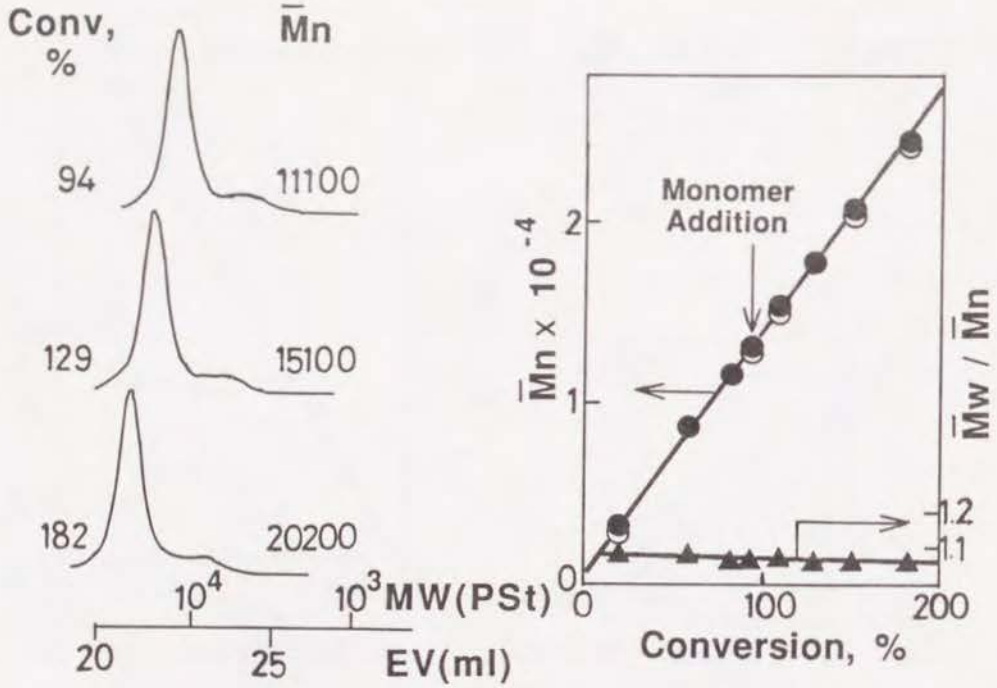
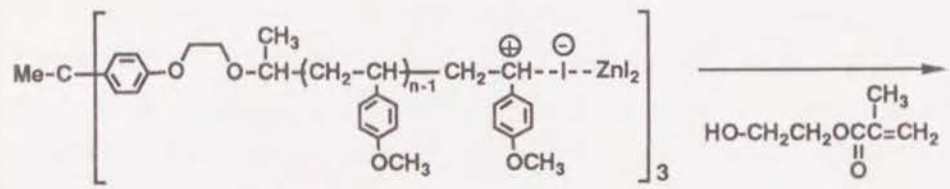


Figure 2. $\bar{M}_n$,$\bar{M}_w/\bar{M}_n$, and MWD of tri-armed star poly(pMOS) obtained with trifunctional initiator (**6**)/ZnI_2 before and after the monomer addition in toluene at -15°C: $[pMOS]_0 = [pMOS]_{added} = 0.38$ M; $[\mathbf{6}]_0 = 3.3$ mM; $[ZnI_2]_0 = 3.3$ mM. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values are for the main peaks seen in the MWD curves; (●,▲) by size-exclusion chromatography with a polystyrene calibration; (O) by ^{1}H NMR (cf. Figure 3).

The living nature of the polymerizations with **6**/ZnI_2 was further demonstrated by so-called "monomer-addition" experiments where feeds of pMOS were added to completely polymerized reaction mixtures (Figure 2). The linear increase in $\bar{M}_n$ and the progressive shift toward high molecular weight in MWD continued after the monomer addition.

2. End-Capping Analysis

In order to confirm the quantitative formation of tri-armed polymers from initiator **6**, the concentration of the living growing ends was measured by end-capping. Thus, the living polymer **7** was terminated with 2-hydroxyethyl methacrylate (HEMA), which is known to react quantitatively and cleanly with the living end to give a methacrylate-capped poly(pMOS) [polymer **8**, Eq (4)].[5] In the living polymerization of pMOS with **6**/ZnI_2, the quenching reaction with a large excess of HEMA also proceeded rapidly and quantitatively.



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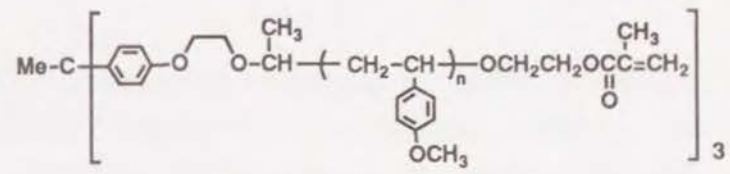


8

Figure 3 illustrates the ^{1}H NMR spectrum of the polymer (**8**) thus obtained after the end-capping reaction. The spectrum shows all key absorptions of the poly(pMOS) main chain (a, b, g and h), the peaks arising from initiator **6** (i – m), and the terminal HEMA residue (c and d), all of which confirm the structure expected for polymer **8**.

The number-average degree of polymerization ($\overline{DP}_n$) of **8** was determined from the peak intensity ratio of the head methyl to the pendant methoxy (a/i) or to the phenyl groups (b/i). As plotted in Figures 1 and 2 with open circles, these absolute $\overline{DP}_n$'s were in good agreement with the calculated values, $[pMOS]_0((\%\ conv.)/100)/[\mathbf{6}]_0$, based on the assumption that one living polymer is formed from

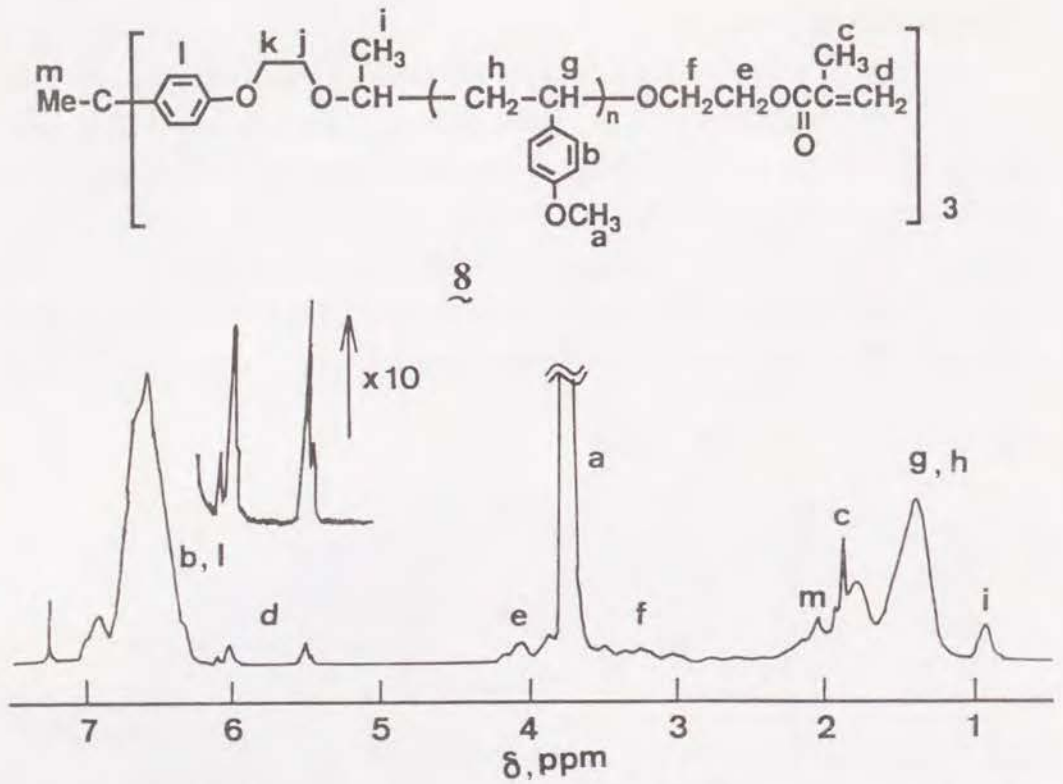


Figure 3. ^{1}H NMR spectra of methacryloxy-capped tri-armed star poly(pMOS) **8**. $[pMOS]_0$ = 0.38 M; $[\mathbf{6}]_0$ = 7.4 mM; $[ZnI_2]_0$ = 3.3 mM; conversion~100%. $\bar{M}_n$ = 7710, $\bar{M}_w/\bar{M}_n$ = 1.06 by size-exclusion chromatography. $\overline{DP}_n$ (calcd) = 51.6 (= $[pMOS]_0/[\mathbf{6}]_0$); $\overline{DP}_n$ (obd) = 52.2 (from a/i) or 53.1 (from b/i). The number of the methacrylate groups per molecule: 3.08 (from e/i) or 2.98 (from d/i).

one molecule of **6**. In both Figures 1 and 2, it should also be noted that the absolute $\bar{M}_n$'s (open circles) by ^{1}H NMR are very close to the $\bar{M}_n$'s (filled circles) by size-exclusion chromatography with a polystyrene calibration.

The number-average end-functionality ($\bar{F}_n$) of the terminal methacrylate for **8** was determined by comparing the integrated ^{1}H NMR peak areas of the head methyl to the methylene (e/i) or to the vinyl group (d/i) arising from the HEMA quencher. Though determined from the intensity ratios independent of each other,

$\bar{F}_n$ was invariably close to three, indicating the formation of methacryloxy-capped tri-armed star poly(pMOS) **8** that has exactly three methacrylate groups per chain (e/i = 3.08 and d/i = 2.98).

Polymer **8** is a trifunctional star-shaped macromonomer with three methacryloxy ends that may find uses, for example, as crosslinking agent, interpenetrating polymer network, and prepolymer for elastomer.

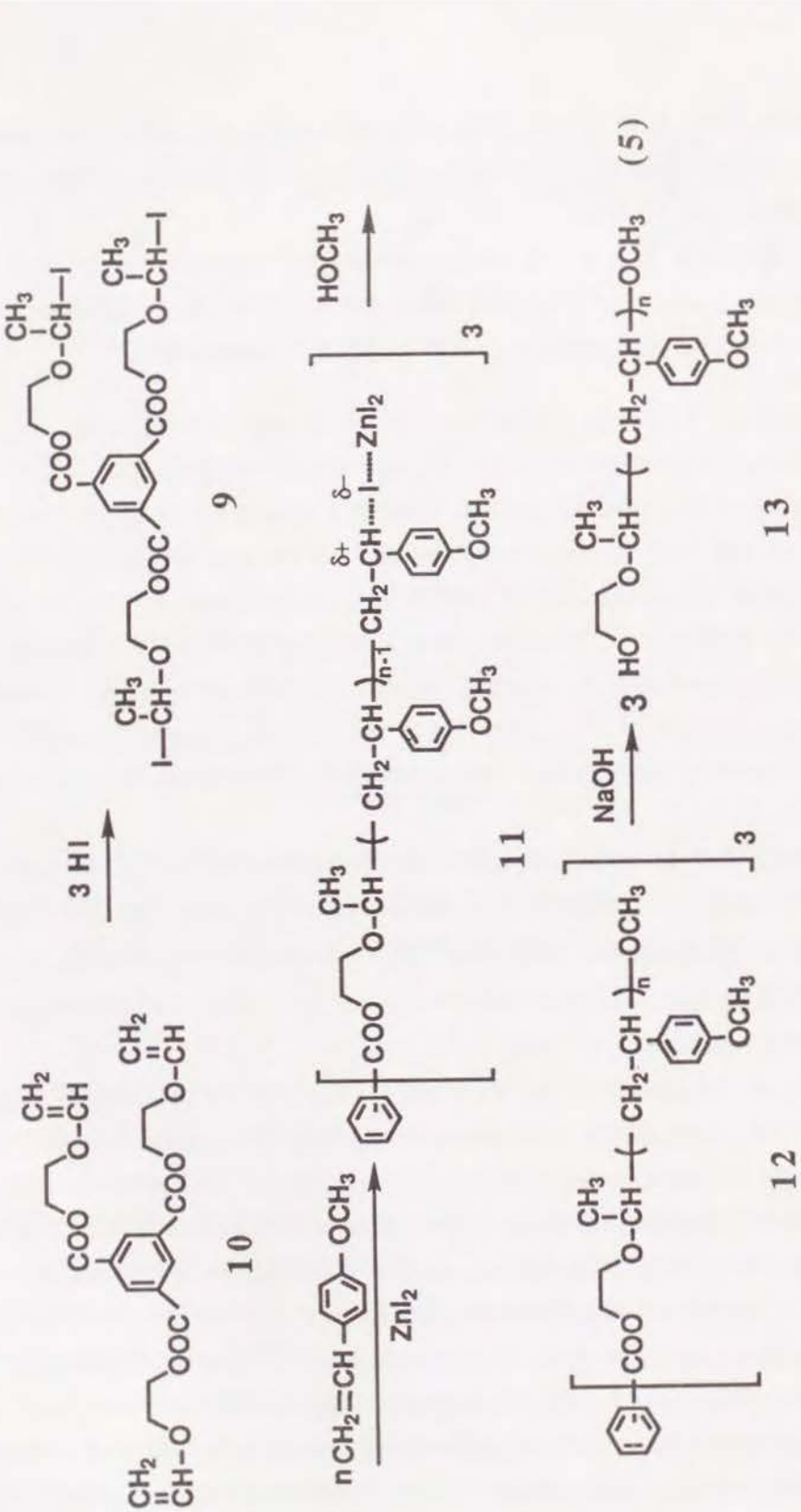
3. Ester-Core Hydrolysis: Uniformity of Three Arm Chains

Besides the existence of three living ends per molecule, the uniformity in length of three arm chains is another important structural factor that should be verified for well-defined tri-armed polymers. To this end, as shown in Eq 4, the living cationic polymerization of pMOS was initiated with a new trifunctional initiator **9**, where three initiating sites (vinyl ether-HI adduct moieties) are connected to an aromatic ring through three hydrolyzable ester bonds. Similarly to the ether-core version **6**, initiator **9** was prepared by quantitative addition of hydrogen iodide across the three double bonds of the corresponding trifunctional vinyl ether **10**.[1]

With ZnI_2 as activator, trifunctional initiator **9** indeed induced polymerization of pMOS in toluene at 0°C and led to living polymer **11**. The MWDs of the products (**12**; quenched with methanol) were very narrow ($\bar{M}_w/\bar{M}_n$ < 1.1), and the $\bar{M}_n$'s (by size-exclusion chromatography) increased in direct proportion to monomer conversion (Figure 4A).

Figure 5A illustrates the ^{1}H NMR spectrum of the product [**12**, Eq (5)]. The spectrum shows all key absorptions of the poly(pMOS) main-chain (a, b, e and f), the peaks arising from initiator **9** (g – k), and the terminal methoxy groups (c and d), all of which confirm the structure expected for polymer **12**. The $\overline{DP}_n$'s for **12**, determined from the peak intensity ratio of the pMOS aromatic ring (peak b) to the terminal methoxy (peak c) or to the initiation residues (peaks g and k), were in good agreement with the calculated values; i. e., $\overline{DP}_n$: calcd ($[pMOS]_0/[HI]_0$, conversion~100%) = 115; obd, 111 (b/c), 109 (b/g), 112 (b/k).

The ester-core moiety of polymer **12** was then hydrolyzed under mild alkaline conditions to detach the arm chains. As shown in Figure 4B, the MWD of



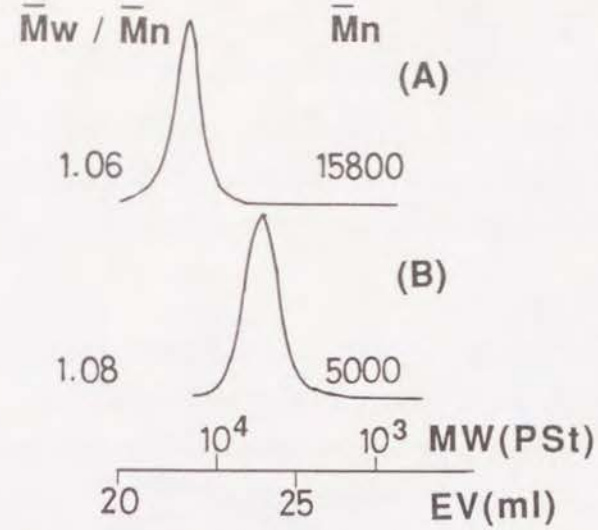


Figure 4. MWD of triarmed star poly(pMOS) **12** (A), obtained with **9**/ZnI_2, and its hydrolysis product **13** (B). Polymerization conditions for **12**: in toluene at -15°C; $[pMOS]_0$ = 0.38 mM; $[\mathbf{9}]_0$ = 3.3 mM; $[ZnI_2]_0$ = 3.3 mM; conversion ~ 100%.

the hydrolyzed polymer (**13**) remained as narrow as that of the original polymer **12** (Figure 4A), and the peak positions cleanly shifted in accordance with the expected molecular weight reduction into one third upon hydrolysis; see the relative $\bar{M}_n$ values shown in Figure 4 based on size-exclusion chromatography.

Figure 5B shows the ^1H NMR spectrum of the hydrolysis product (from the sample of **12** shown in Figure 5A). Comparison between spectra 5A and 5B shows the complete conversion of the tri-armed star polymer **12** into a linear arm polymer (**13**) that carries a hydroxy terminal derived from the ester core. Namely, signals j and k in Figure 5A, due to the ester core, are absent in Figure 5B. The $\overline{DP}_n$ of this sample as determined from the pendant phenyl/terminal methoxy ratio (b/c = 36,7), which was nearly one third of the overall $\overline{DP}_n$ (= 115) of the precursor **12**.

Figures 4 and 5, therefore, give direct experimental evidence for the well-controlled tri-armed structure of polymer **12**; namely, it possesses exactly three arm chains with a uniform and controlled length.

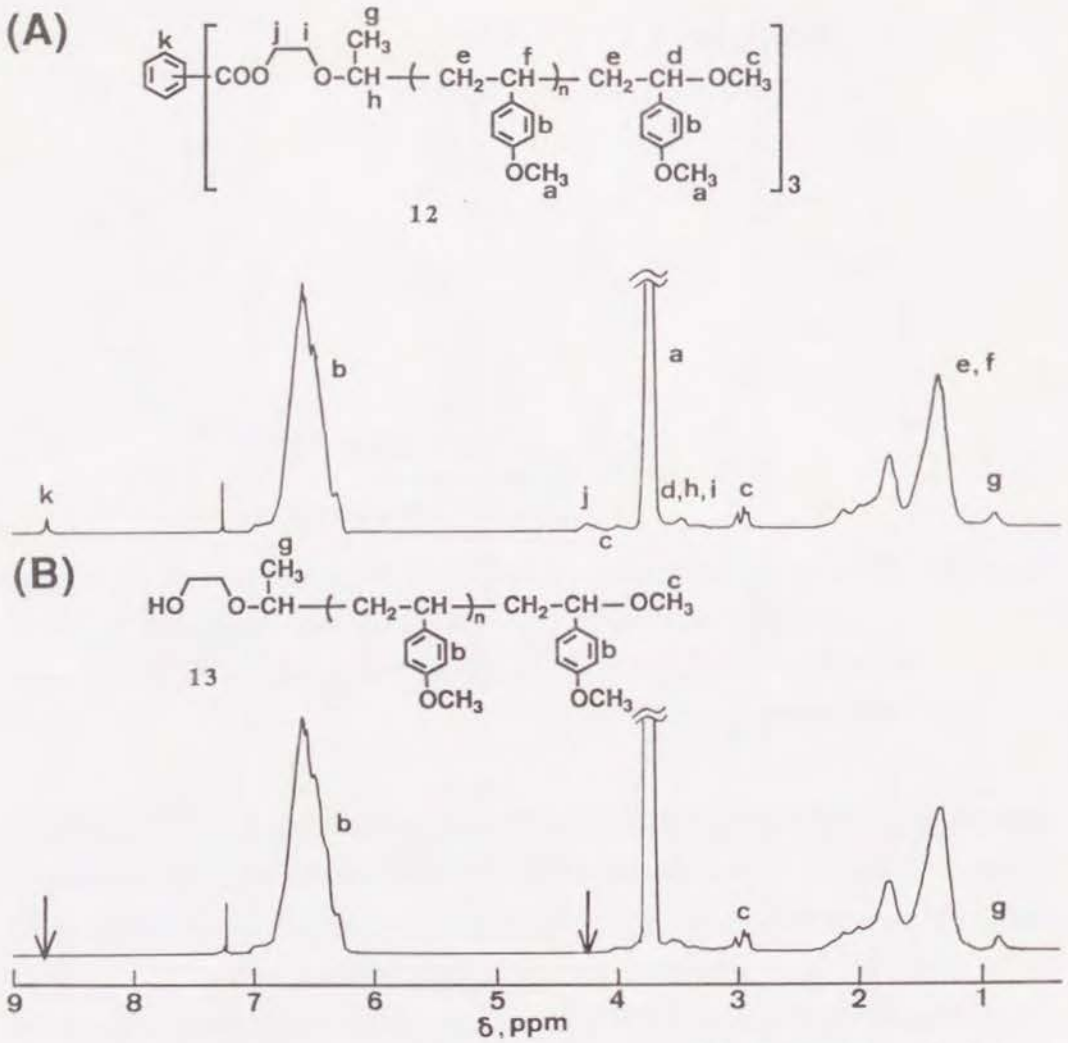


Figure 5. ^{1}H NMR spectra of tri-armed star poly(pMOS) **12** (A) its hydrolysis product **13** (B). See Figure 4 for the synthesis conditions.

EXPERIMENTAL

Materials

pMOS was purified as described in Chapter 3.[5] Trifunctional vinyl ethers, **1** and **10**, were synthesized and purified as described.[1] Other chemicals, including hydrogen iodide and ZnI_2, were purified and used as reported.[3,6]

Procedures

Polymerization of pMOS was carried out under dry nitrogen in a baked glass vessel equipped with a three-way stopcock. Trifunctional vinyl ether **1** (66 mM in 0.25 mL toluene) was first treated with 3 equivalents of hydrogen iodide in *n*-hexane (0.25 mL) at -78°C to give initiator **5** [Eq (3)]. To this was added solutions of pMOS (in toluene, 4.0 mL) and ZnI_2 (in diethyl ether, 0.50 mL) in this order: $[pMOS]_0$ = 0.38 M; $[\mathbf{5}]_0$ = 3.3 mM; $[ZnI_2]_0$ = 3.3 mM. The mixture was allowed to stand at -78°C for 20h and then transferred to a methanol bath kept at -15°C to initiate polymerization. The living polymerization with another initiating system, **9**/ZnI_2, was carried out in the same way except for replacement of trifunctional vinyl ether **1** with **10** [Eq (5)]. Hydrolysis of polymer **12** [Eq (5)] was described before.[1]

Polymer Characterization

The MWD of the products was determined by size-exclusion chromatography in chloroform at room temperature on a Jasco Trirotar chromatograph equipped with polystyrene gel columns (Shodex K-802, K-803 and K-804: 8.0 mm i.d. x 300 mm each) and refractive index/ultraviolet dual detectors. The apparent number-average molecular weight ($\bar{M}_n$) and the polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from size-exclusion eluograms on the basis of a polystyrene calibration. The structure and the absolute $\bar{M}_n$ of the polymers were determined by ^{1}H NMR operated at 270MHz in $CDCl_3$ at +40°C on a Jeol GSX-270 spectrometer.

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LIST OF PUBLICATIONS

CHAPTER 1	*Polym. Bull.*, **21**, 357 (1989)
CHAPTER 2	*Macromolecules*, in press.
CHAPTER 3	*Macromolecules*, in press.
CHAPTER 4	*Makromol. Chem.*, in press.
CHAPTER 5	*Macromolecules*, **24**, 4926 (1991)
CHAPTER 6	*Polym. Bull.*, **25**, 529 (1991)
CHAPTER 7	*Makromol. Chem.*, in press.

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December, 1991

Hajime Shohi